PB-214 605

Hollow Fiber Technology for Advanced Waste Treatment

Chemstrand Research Center, Inc.

prepared for
Environmental Protection Agency

DECEMBER 1972

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EPA-R2-72-103
DECEMBER 1972

Environmental Protection Technology Series

PB 214 605

Hollow Fiber Technology for Advanced Waste Treatment

Office of Research and Monitoring
U.S. Environmental Protection Agency
Washington, D.C. 20460

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SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

3. Accession No. **W**

4. Title: **Hollow Fiber Technology For Advanced Waste Treatment**

5. Report Date: **November 1971**

6. Performing Organization Report No.

7. Author(s): **J. D. Bashaw, J. K. Lawson, and T. A. Orofino**

9. Organization: **Monsanto Research Corporation**
Chemstrand Research Center, Inc.
Durham, North Carolina

10. Project No.: **17040 FEE**

11. Contract/Grant No.: **14-12-926**

13. Type of Report and Period Covered

15. Supplementary Notes: **Environmental Protection Agency report number, EPA-R2-72-103, December 1972.**

16. Abstract

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This report was submitted in fulfillment of Contract 14-12-926, under the sponsorship of the U. S. Environmental Protection Agency.

17a. Descriptors: ***Reverse osmosis, *Desalination processes, *Membranes, Wastewater treatment, Semi-permeable membranes**

17b. Identifiers: ***Hollow fiber technology, *Cellulose acetate hollow fine fibers, fiber spinning, hollow fiber modules**

17c. COWRR Field & Group: **05D**

18. Availability

19. Security Class. (Report)

20. Security Class. (Page)

21. No. of Pages: **91**

22. Price

Send To:
WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

Abstractor: **J. D. Bashaw**

Institution: **Monsanto Research Corporation**

WRSIC 102 (REV. JUNE 1971)

U. S. GOVERNMENT PRINTING OFFICE : 1972 724-770/169

EPA-R2-72-103
December 1972

HOLLOW FIBER TECHNOLOGY FOR ADVANCED WASTE TREATMENT

by

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U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

SOD No. EP 1.23/2:72-103 (#1.25)

EPA Review Notice

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ABSTRACT

The utility of hollow fiber reverse osmosis membranes in renovation of secondary municipal effluent was investigated through construction, laboratory evaluation, and monitoring in field service of various hollow fiber modules. All units incorporated cellulose acetate hollow fibers, annealed for sodium chloride rejections of 80-95% at 250 psi external operating pressure. Product water capacities ranged from 50-300 gallons per day. Module designs considered included the single seal end, looped fiber bundle; double seal end, parallel bundle; radial flow parallel bundle; and a rolled, woven hollow fiber fabric. The typical flux-rejection characteristics of the basic fiber system (4 gfd-95%) were observed in waste water service, but steady-state flux, maintained only with regular detergent flushes, was usually less than 1 gfd, with an accompanying decline in selectivity. A notable exception was the woven hollow fiber fabric design, which showed improved retention of start-up characteristics and minimum effects of shell-side fouling during short-term field tests.

This report was submitted in fulfillment of Contract 14-12-926, Project #17040 FEE, under the sponsorship of the Environmental Projection Agency by the Monsanto Research Corporation, Chemstrand Research Center, Inc., Box 731, Durham, North Carolina 27702. The Project Engineer was J. D. Bashaw.

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I CONCLUSIONS

In general, two facts seem evident from operations with the series of hollow fiber modules tested in wastewater service. First, efficiency of module operation is definitely a function of the efficiency of module cleaning and the degree of module cleanliness maintained. Best results were almost always obtained with modules recently subjected to a detergent treatment in the field, or with those which had been renovated in the laboratory and returned to service. Our results also indicate that a systematic cleaning and conditioning regime in the field promotes improved module performance. Possibly the best evidence for this conclusion is to be found in the performances of modules D010 and D008.

A second, significant observation is that module designs which promote a smooth, regular flow of water through the unit, with minimum opportunity for packing or channeling, are likely to give improved performance, both with respect to flux stability and efficiency of rejection over an extended time. The primary evidence for this generalization is the field performance of module WA001. The woven fabric concept, which this unit represents, appears to be an attractive way of achieving uniform, low resistance shell-side flow, while still retaining the desirable aspects of hollow fiber geometry. With fibers of dimensions used in this program, the woven fabric design permits a ratio of effective membrane area to pressure vessel volume of approximately 1000 ft^2/ft^3 - still an order of magnitude larger than for flat membrane designs.

The frequently noted failure of BOD rejection results to turn out like those from sodium ion or chloride ion analysis was a source of some concern in our work. In a number of specific cases, we seemed to be dealing with indications that cellulose acetate fiber is more permeable to such gases as chlorine or hydrogen sulfide than it is to water. Accumulation of hydrogen sulfide or other oxidizable gases in the product water would have the net effect of indicating poor performance with respect to BOD rejection.

II RECOMMENDATIONS

The principal objective of this program was evaluation of various hollow fiber configurations in renovation of waste water by reverse osmosis. On the basis of the exceptionally good performance shown by units incorporating the woven fabric configuration, it is recommended that this module concept be further investigated.

The woven fabric design specifically investigated in this program could be immediately improved in subsequent versions. First, it is likely that smaller, and more durable warp fibers could be employed. Second, overall module efficiency could be improved by reduction in the diameter of the center mandrel.

The results obtained here, more broadly interpreted, indicate that hollow fiber bundles providing uniform, low-resistance shell-side flow are much less prone to fouling in sustained service. This advantage is gained at the expense of a substantial reduction in fiber packing density. Accordingly, it seems worthwhile to investigate the utility of related, structured fiber assemblies in order to retain the desired hydraulic characteristics, with potential for improvement in packing density.

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III INTRODUCTION

This report provides a detailed account of all work carried out from 15 October 1970 to 30 November 1971 under Contract 14-12-926, granted to Monsanto Research Corporation by the Water Quality Office, U. S. Environmental Protection Agency. The objective of the program was to evaluate the utility of high-flux hollow fibers in treatment of secondary municipal effluent. Essentially no development work on preparation of hollow fibers was conducted under this contract, although current results and improvements from other related programs receiving U. S. Government support were utilized whenever applicable. The organization of the report follows the technical approach originally proposed and carried out: laboratory evaluation of the basic cellulose acetate hollow fiber system in rejection of waste water constituents; design and construction of modules to meet the requirements of waste water service; laboratory research and engineering studies of fouling phenomena to aid in module design and operation; evaluation of module designs in field service and selection of appropriate operation and maintenance procedures.

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IV LABORATORY CHARACTERIZATION OF HOLLOW FIBER PERFORMANCE

The hollow fiber system available at the beginning of this program was a dry-jet wet spun cellulose acetate composition, typically 300/100 micron OD/ID dimensions, capable of being annealed to provide a range of flux-rejection properties at 250 psi. Later in the program, a modified cellulose acetate hollow fiber was developed to provide especially attractive flux-divalent ion rejections at 100-150 psi. Laboratory test facilities were constructed to evaluate fiber performance in rejection of sodium chloride; phosphate, nitrate, and acetate ion; ammonia, urea, glycine, glycols and detergents.

Preparation of Hollow Fibers

The basic cellulose acetate fibers used in this program are essentially a hollow fiber form of the density-gradient or skin-core Loeb[1] membrane structure. By virtue of the very thin, dense skin formed on the outer surface of the hollow fiber, rejection of dissolved solutes may be raised to a high level (98%, for example, with sodium chloride). The bulk of the hollow fiber wall is a relatively porous structure which easily transports product water. Thus, the only appreciable resistance to passage of water through the fiber wall is that created by the salt-rejecting skin. Since the transport rates of both salt and water are inversely proportional to skin thickness, decrease in the latter does not alter the rejection capability; product water flux, on the other hand, is correspondingly increased. In the preparation[2] of hollow fibers incorporating this desirable structure, considerable latitude is afforded by the unique spinning process in control of skin thickness and degree of perfection. As a result, the methods developed permit trade-off in flux and rejection over a wide range. Cellulose acetate hollow fibers under sustained test at 250 psi external pressure with 3000 mg/l sodium chloride feed typically provide from about 2 gal/ft^2/day product water flux (gfd) with 98% salt rejection to 10 gfd with 50% salt rejection. A particularly useful intermediate selection is 4 gfd with 95% rejection. Both flux and rejection increase with pressure over the permissible range (maximum 350 psi).

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The basic steps in the continuous solution spinning process are analogous to those customarily employed in Loeb membrane preparation. The spinning dope consists of about 35% cellulose acetate dissolved in a mixture of acetone and formamide. Various proportions are suitable for spinning - including cellulose acetate in pure acetone - depending upon the selection of other process parameters. A typical composition of polymer, acetone and formamide is 35:20:30 by weight.

The viscous spinning dope is metered through a thermostated jacket and extruded through a hollofil spinnerette. The spinnerette may be of several basic designs, including a segmented arc and a tube-in-orifice arrangement. The latter provides greater flexibility in control of fiber diameters; the chief virtue of the former is its easier adaptability to multihole spinnerette construction. With both types, the outside diameter of the hollow fibers extruded may be made substantially less than that of the orifice opening by increasing the take-up rate on the thread line.

The first important step in the formation of the actual membrane filament occurs after emergence of the hollow fiber from the orifice and during passage through an air gap. The evaporation of the volatile component (acetone) which occurs establishes the concentration gradient essential for skin formation. The continuous thread line, partially stabilized by passage through the evaporative air gap, next enters the coagulation bath - usually water at low temperature. Most of the solvent near the fiber outer surface is replaced by water in this process, precipitating the polymer and stabilizing the fiber. Virtually complete removal of solvent and final stabilization of the hollow fiber occurs in subsequent passage through water wash baths on godet rolls.

The final tailoring of membrane properties is obtained through consolidation of the fiber wall structure in post or in-line immersion in hot water. The hollow fibers, which must be maintained wet in storage and subsequent operations, are now wound on bobbins and are ready for use in construction of reverse osmosis modules.

Cellulose acetate hollow fibers spun by minor variants of the above procedures have been tested under a wide variety of end-use conditions. Fibers ranging in outside diameter from about 100 to about 300 microns have been prepared. Typical rejections of sodium chloride have been cited earlier; in general, a given fiber shows much improved rejection of phosphate, sulfate and other multivalent ions. Rejection of all solutes at 250 psi is essentially constant for feeds ranging from 1000

to 10,000 mg/l. Flux stability is generally quite good and has been established in continuous reverse osmosis testing for periods exceeding two years.

Construction of Test Facilities

An eight-cell reverse osmosis test loop was assembled early in the program, to permit characterization of small fiber bundles and, in later work, to accommodate 100-200 gpd modules for process investigation. Key components of the test loop included: two independent feed systems to permit changing feed compositions with no down-time, a Milton-Roy duplex diaphragm positive displacement pump rated at 12.6 gph, and a dome-loaded diaphragm back pressure regulator of our own design. Extensive use was made of PVC conduits, to minimize accumulation of iron deposits in the recirculation system. A schematic of the laboratory test loop is given in Figure 1.

The standard fiber test bundle consists of a supported loop of 30 wraps of hollow fibers (60 fiber ends), potted into a 1/8" pipe nipple with an epoxy resin (Shell Epon 815® and curing agent T-1®). The pipe nipple is installed in the test loop, through which feed solution can be circulated at 200-400 psi, in contact with the exterior surfaces of the hollow fibers. Flux (in gfd) is obtained by measuring volume of product water from the fiber bundle of known surface area per unit time; rejection r by conductivity or chemical analysis of feed stream composition (C_f) and product composition (C_p), in accordance with the relationship

$$r = 100 (1 - C_p/C_f).$$

Performance with Key Solutes

Laboratory reverse osmosis test facilities were utilized in evaluation of flux and rejection of hollow fiber samples with aqueous solutions of solutes representative of those in municipal waste water. All experiments were conducted with the small fiber bundles described in the preceding section, at ambient temperatures, and at essentially zero recovery. The hollow fibers tested were cellulose acetate, spun from 40:60 acetone:formamide, and annealed at various temperatures to provide a range of flux-selectivity relationships. A summary of results is given in Table I.

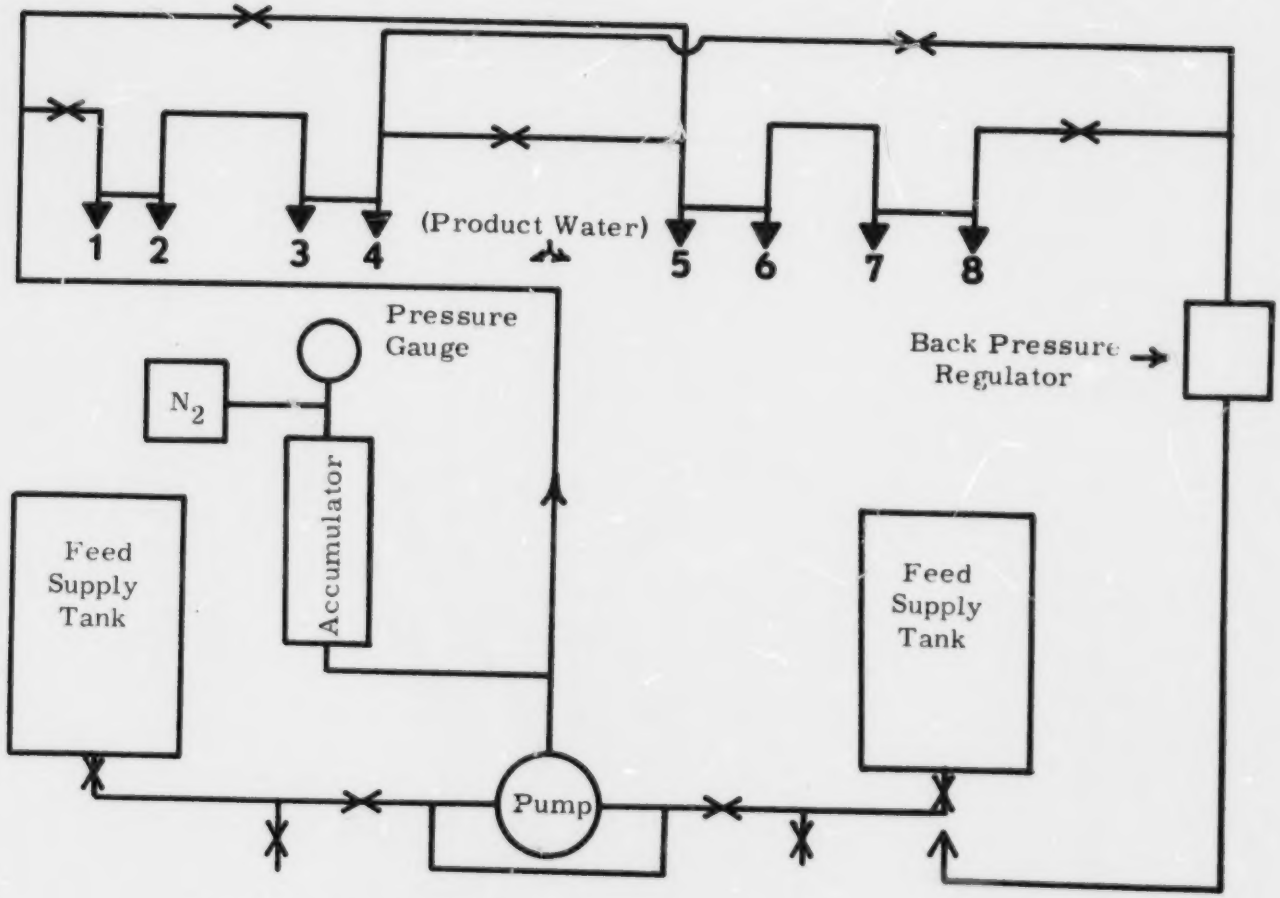

Figure 1. Schematic of laboratory reverse osmosis test loop for hollow fiber units

TABLE 1

Summary of Reverse Osmosis Performance for 40:60 Cellulose Acetate Hollow Fibers at 250 psi

Annealing Temperature ° C	Flux gfd	Rejection, % NaCl (pH 6.1)	orthophosphate (pH 7)	nitrate (pH 6.1)	acetate (pH 6.6)	ammonia (pH 6.6)	urea (pH 5.9)	glycine (pH 6)
75	7.0	86	98	68	82	80	15	89
78	6.3	92	99	81	91	90	16	93
82	4.4	95	(100)	92	93	90	19	97
85	3.7	97	(100)	93	97	94	25	99
87	3.0	98	(100)	93	95	97	28	(100)

Continuous testing for extended periods was confined to experiments with sodium chloride feed at 1000 mg/l. Stability of both product water flux and selectivity was good over the total test period of approximately three months. By about the sixtieth day of operation, substantial flux decline had occurred, especially with fiber samples annealed at lower temperatures (higher flux samples). However, a thirty-minute low-pressure flush with 2% citric acid solution removed ferric hydroxide, accumulated from the test loop, and restored performance. Details of the sodium chloride test sequence are given in Table 2.

The first solute of specific interest in advanced waste treatment to be investigated was the orthophosphate ion. The feed solution was prepared from NaH_2PO_4 with phosphoric acid added to adjust the feed pH in the range of 4.0 to 7.0. Phosphate rejection varied from 96.7% for fiber annealed at 75° C at a pH of 4.0 to greater than 99.9% for fiber annealed at 87° C over the whole pH range investigated. The results obtained at a feed pH of 7.0 are given in Table 3. Phosphate was determined colorimetrically by spectrophotometric absorption at 705 mμ of the color developed with ammonium molybdate.

At lower pH, there was a slight loss in selectivity to orthophosphate (especially for fiber annealed at 75 and 78° C) due to the existence of more undissociated phosphoric acid at lower pH. Since the rejection is quite high for all samples, the effect of this loss of selectivity on rejection is quite small. However, the "salt reduction factor," C_f/C_p (C_f = feed concentration, C_p = product concentration), is sensitive to small changes in selectivity. This is illustrated in Table 4. Similar trends were observed for all fiber samples which were sufficiently permeable to orthophosphate to give a detectable product concentration. Although the effect of pH on selectivity to orthophosphate was slight, the fact that there was any effect at all suggested that pH would be a very important variable in the case of weak acids and bases, such as, acetic acid and ammonia.

Another solute of specific interest in advanced waste treatment is the nitrate ion. The standard 40:60 hollow fibers examined in this phase of the program showed good selectivity toward sodium nitrate, but less so than toward sodium chloride. Rejections for hollow fibers annealed at different temperatures are given in Table 5.

The rejection of sodium acetate (as a model organic solute) was determined in the pH range 4.0 to 6.6. As expected, rejection was a strong function of pH, ranging from 33% at pH 4.0 to 95% at pH 6.6

TABLE 2

Dependence of Product Water Flux on Time for Cellulose Acetate Hollow Fibers Operating with 1000 mg/l NaCl at 250 psi and Zero Recovery

Days	Flux, gfd				
	813-3-75	813-3-78	813-3-82	813-3-85	813-3-87
1	7.56 (86.1)[a]	6.31 (92.5)	4.37 (96.4)	3.45 (97.7)	2.74 (98.8)
4	6.94	6.15	4.05	3.51	2.75
11	5.70	5.70	4.03	3.67	2.46
32	6.71	6.28	4.43	3.82	3.00
52	5.55	6.08	4.59	4.11	(54)[b] 2.89
65	4.41 (74.2)	4.82 (87.2)	3.99 (92.9)	3.67 (96.9)	(62) 2.71 (95.4)
70	Samples cleaned with 2% citric acid				(67)
72	6.81 (83.2)	6.37 (91.8)	4.54 (93.6)	3.77 (97.2)	(69) 3.00 (98.2)
74	6.28 (83.8)	5.94 (92.8)	4.25 (94.2)	3.57 (97.8)	(75) 2.75 (97.8)

[a] Rejection of 1000 mg/l NaCl.

[b] Operating days for Sample 813-3-87.

TABLE 3

Rejection of Orthophosphate by Cellulose Acetate Hollow Fibers

250 psi, feed pH = 7.0, 1600 mg/l PO_4^{-3}

Sample	Product Concentration, mg/l	Rejection, %
813-3-75	38	97.6
-78	13	99.1
-82	2	99.8
-85	1	>99.9
-87	<1	>99.9

TABLE 4

Effect of pH on Orthophosphate Rejection

Sample 813-3-75, 250 psi

pH	C_f/C_p	Rejection, %
7.0	42.0	97.6
6.0	38.7	97.4
5.0	36.8	97.3
4.0	30.6	96.7

TABLE 5

Rejection of Nitrate by Cellulose Acetate Hollow Fibers

1000 mg/l $NaNO_3$ at 250 psi

Sample	Rejection, %
813-3-75	68
-78	81
-82	92
-85	93
-87	93

for the fiber sample annealed at 87° C. The data are summarized in Table 6. To the extent that organic carbon in secondary effluents is present in the form of short-chain carboxylic acids, the results indicate an operation pH near neutrality would be desirable.

The acetate ion feed solution described above also contained 50 mg/l of ammonia. Rejections for this constituent are given in Table 7. Selectivity in this case is also pH dependent, but much less so, owing to the predominance of ammonium ion in the pH range examined.

The laboratory hollow fiber test series was also extended to examination of urea rejection. Analysis was by the Kjeldahl method, data supplied by the University of North Carolina Water Research Laboratory. The results are summarized in Table 8. Selectivity of all fiber samples toward urea was found to be poor, a result which appears to be characteristic of cellulose acetate membrane systems reported in the literature also.

A similar test series on glycine solutions, representative of some amino acid constituents in waste water, was also completed. Analysis was done by spectrophotometry of the glycine complex with cupric ion in the UV spectrum (work done at Chemstrand Research Center). Results

TABLE 6

Acetate Rejection as a Function of pH for Cellulose Acetate Hollow Fibers, 250 psi

Sample	Rejection, %[a]			
	pH = 4.0	5.0	6.1	6.6
813-3-75	25	69	75	82
-78	28	74	86	91
-82	28	75	87	93
-85	< 0 ?	76	90	97
-87	33	77	91	95

[a] Analyzed as organic carbon by the University of North Carolina Water Research Laboratory, Chapel Hill, North Carolina.

TABLE 7

Ammonia Rejection by Cellulose Acetate Hollow Fibers, 250 psi

Sample	Minimum-Maximum % Rejection
813-3-75	72-84
-78	83-92
-82	81-90
-85	86-94
-87	93-97

TABLE 8

Reverse Osmosis Performance of Cellulose Acetate Hollow Fibers with Urea Feed Solutions

(Approximately 500 mg/l feed at 250 psi and 26° C)

Sample	Run #1		Run #2	
	Flux, gfd	r, %	Flux, gfd	r, %
813-3-75	6.2	16	5.5	9
-75	5.6	16	5.6	14
-78	5.9	17	5.6	14
-78	5.6	22	5.3	12
-82	4.4	22	4.3	16
-85	3.8	29	3.7	20
-87	3.1	33	2.9	23
-92	2.1	33	2.0	28

Note: The apparent variation in urea selectivity between the two runs is unexplained. Possibly, an error in feed concentration is responsible.

are given in Table 9. Rejection is seen to be quite good, as might be expected for a highly polar zwitterion compound.

Subsequent laboratory characterization of the hollow fiber test series included runs with aqueous solutions of poly(ethylene glycol)-600 and Triton X-100. Flux-time data are given in Table 10. The object of this work was to identify differences in flux decline which should be associated with surface activity of the solute species. In the PEG-600 runs, flux decline was negligible over the 80-hour test period. This solute presumably establishes an equilibrium concentration in the membrane (fiber wall) rather quickly, which dictates subsequent transport of solute and water in sustained operation. With Triton X-100, significant flux decline was noted, particularly with the higher-flux fibers. As one might postulate, the polar/non-polar asymmetry of the molecule in this case appears to promote partial solubility of the solute at the membrane surface, with attendant accumulation and surface fouling. Recent results [3] suggest that such effects are an important aspect of fouling in practical applications of reverse osmosis to waste water renovation.

TABLE 9

Reverse Osmosis Performance of Cellulose Acetate Hollow Fibers with Glycine Feed Solutions

(Approximately 500 mg/l feed at 250 psi and 26° C; pH 5.8-6.3)

Sample	Flux, gfd	r, %
813-3-75	5.8	89
813-3-78	6.2	93
813-3-82	4.5	97
813-3-85	3.5	99
813-3-87	2.9	99.6
1302-82	2.2	98
1302-85	1.8	99
1302-88	1.0	99.6

The flux-pressure response in such systems is a more direct measure of surface fouling and these effects were also examined. Results are given in Table 11. Although there is some departure of the flux-pressure response from linearity (a linear relation would be expected, because of the negligible osmotic pressure of the feed), the effects are small and could easily be obscured by normal compaction.

It appears from work completed to date that surface active agents contribute to flux decline in our hollow fiber systems, but much less so than anticipated from results on flat membranes. We have established from detailed theoretical analyses of flow in hollow fiber systems, and confirmed in practice, that salt polarization is also very much less of a problem with hollow fiber units. Thus, it is reasonable to conclude that the secondary membrane built up by convection of surface active agents to the primary membrane surface is less easily formed in hollow fiber units. In subsequent laboratory work (cf. Section VI), however, the effects of surface active solutes on prototype modules, operating at more realistic end-use conditions, were also investigated.

TABLE 10

Flux-Time Response of Cellulose Acetate Hollow Fibers with Selected Solutes

Operating Time (hours)	Flux (gfd) for Various Fiber Samples						
	813-3-75	813-3-78	813-3-82	813-3-85	1302-82	813-3-87	1302-88
	1000 mg/l PEG-600 at 250 psi						
Control*	6.7	6.3	5.3	4.2	3.4	3.3	1.18
1	6.3	6.0	5.0	4.0	3.3	3.1	1.18
4	6.4	6.1	5.0	4.0	3.4	3.2	1.18
80	6.2	5.9	4.8	4.0	3.3	3.1	1.15
83	6.2	6.0	4.8	4.1	3.3	3.2	1.13
	500 mg/l Triton X-100 at 250 psi						
Control*	7.2	6.7	4.8	-	3.5	3.0	1.05
1	7.0	6.4	4.8	5.6	3.5	3.1	1.11
2	6.9	5.4	4.7	5.3	3.0	3.1	1.07
3	6.5	5.8	4.8	3.7	3.0	2.9	1.18
4	5.8	5.3	4.0	3.1	2.9	2.7	0.96
21	6.3	5.6	4.3	3.6	3.0	2.8	1.03
23	5.6	5.0	3.8	3.2	2.7	2.4	0.89

TABLE 10 (continued)
Flux-Time Response of Cellulose Acetate Hollow Fibers with Selected Solutes

Operating Time (hours)	Flux (gfd) for Various Fiber Samples						
	813-3-75	813-3-78	813-3-82	813-3-85	1302-82	813-3-87	1302-88
Increase to 1000 mg/l Triton X-100 at 250 psi							
25	6.0	5.4	4.0	3.3	3.0	2.7	1.06
29	5.9	5.5	4.1	3.4	2.8	2.6	0.96
46	6.1	5.6	4.2	-	3.0	2 8	1.04
52	5.9	5.4	4.2	3.4	2.9	2.8	1.07
69	6.0	5.4	4.2	3.9	3.0	2.8	1.04
73	6.1	5.3	4.1	3.4	3.0	2.8	1.C7

* Run with deionized water at 250 psi.

TABLE 11

Normalized Flux-Pressure Results for Cellulose Acetate Hollow Fibers with Triton X-100 Feed

(500 mg/l at 21° C)

Sample	Flux, gfd at 250 psi	10^2 gfd/psi at various pressures				
		50	100	150	200	250
813-3-75	4.97	2.12	2.22	2.23	2.02	1.99
813-3-78	4.88	2.14	2.22	2.11	1.97	1.95
813-3-82	4.15	1.66	1.85	1.76	1.64	1.66
1302-82	2.80	1.18	1.36	1.31	1.34	1.12
813-3-87	2.69	1.10	1.25	1.14	1.09	1.08
1302-88	0.99	0.37	0.49	0.41	0.39	0.40

V DESIGN AND CONSTRUCTION OF HOLLOW FIBER MODULES

A major objective of this program was to evaluate the effectiveness of various hollow fiber module designs in wastewater service. Four basic module design concepts, illustrated schematically in Figure 2, were evaluated in the laboratory; three of these were checked out in field service. In addition, variations in fiber packing density and in arrangement of feed entrance ports were included in the basic designs examined. All designs involved feed stream pressurization on the outside of the hollow fibers, with product water flowing through the fiber bores.

Basic Assembly Techniques

Each of the four module designs represented in Figure 2 involves a parallel bundle of hollow fibers, one or both ends of which are embedded in an epoxy tubesheet. The hollow fibers are wet spun and must be maintained in the wet state throughout module assembly. Accordingly, a number of procedures for construction of the units are identical for all designs.

The first step involves the assembly of as-spun, five-filament, hollow fiber yarn taken from bobbins into hollow fiber bundles. For Designs 1, 2, and 3 of Figure 2, this involves winding hollow fiber yarn onto a suitable mandrel, meanwhile keeping the yarn supply and the bundle moist with water sprays. Design 4 entails a fabric weaving operation, also done in such a way that the emerging fabric can be kept moist.

With all four designs, in the course of bundle assembly, a secondary or dam seal of water compatible, Dow Corning RTV ® bonds the fibers together at a point just below the (subsequent) location of the epoxy main seal(s). This operation divides the fiber bundle into two (or three) parts: the main, active fiber portion and the end portion(s) above the RTV seals.

The next step involves treatment of the fiber bundle end portion(s) with 100° C water, to stabilize the outer fiber diameter against later shrinkage during end-drying. Then, the active fiber portion of the bundle is immersed in gelatin solution and cooled to solidify the gelatin.

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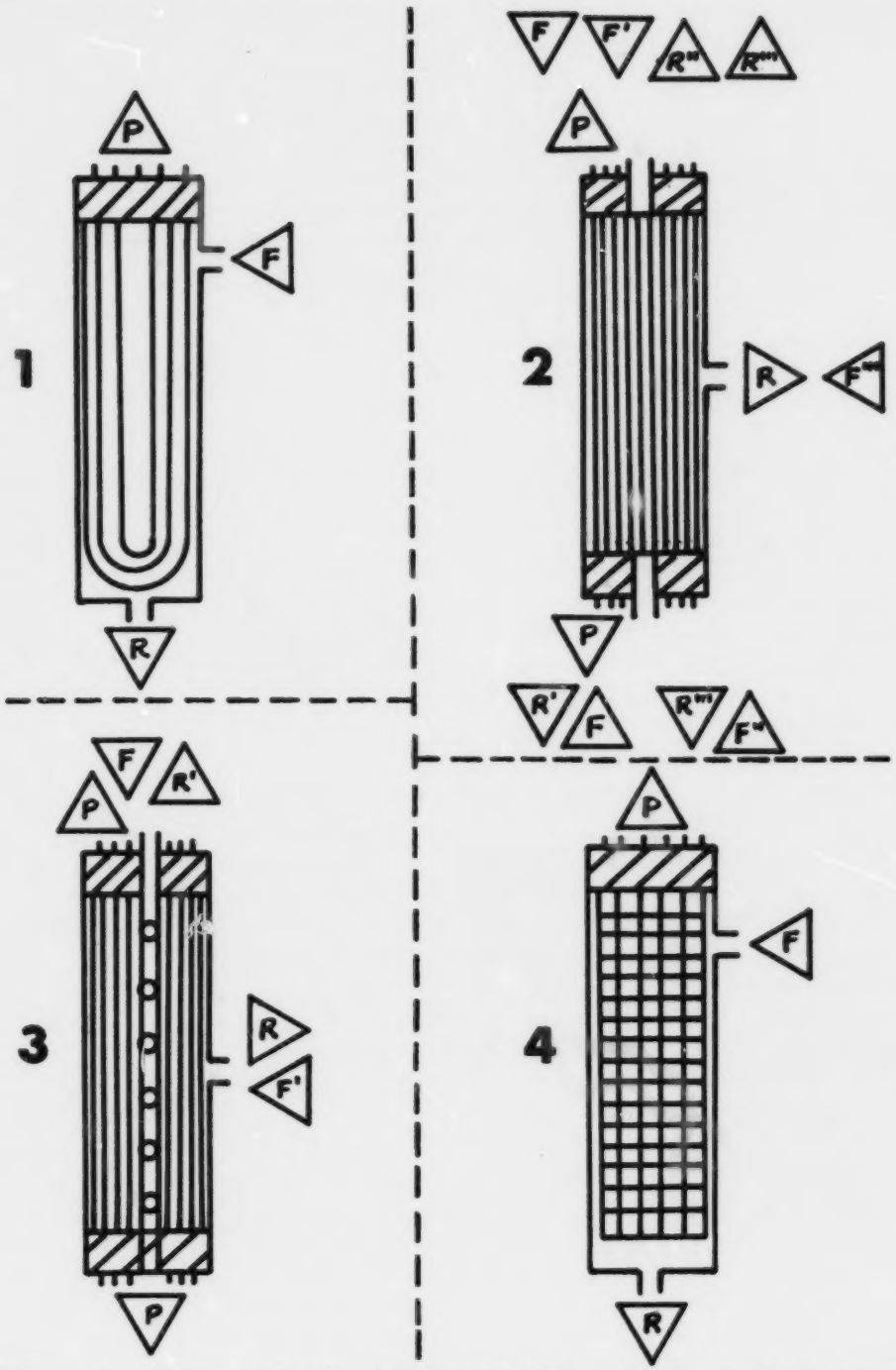

Figure 2. Schematic of basic hollow fiber module designs: 1-single seal looped fiber (Series D); 2-double seal parallel fiber (Series D-2); 3-radial flow (Series R); 4-woven rolled fabric (Series W). Feed, product, and reject flows are indicated by F, P, and R, respectively, with optional combinations indicated by primes.

This operation holds sufficient moisture in the active fiber bundle to retain the reverse osmosis properties, yet immobilizes this water from wicking along the bundle length. Next, the water from the end portion(s) is removed by air drying and the necessary high pressure tubesheets are cast, sealing the fiber bundle to the pressure vessel. The gelatin may now be removed by warm water washing and the bundle is ready for insertion into the rest of its pressure vessel.

Series D: Single Seal Looped Fiber

The basic design of Series D modules is that depicted in Figure 2, Design 1. This is, perhaps, the simplest arrangement of hollow fibers and served as a point of reference in our work. In this concept, hollow fiber is laid down precisely onto a mandrel, to form a closely packed, parallel array of fibers looped at each end. Packing factors (fractional cross-sectional area of pressure vessel filled with fibers) can range up to 0.70. One looped end remains in the final module. The other is severed after the tubesheet is cast to expose the fiber bores for product water removal. Feed enters the bundle under pressure just below the seal area, most conveniently by means of a Victaulic® side-entry coupling. The feed stream flows axially through the bundle, emerging as concentrated brine from the end of the pressure vessel. Product water, passing through the wall of each hollow fiber, travels upward along the fiber bore and exits at atmospheric pressure. A typical Series D design is detailed in Table 12, in this case for Module Number D009, one of those utilized in field service (cf. Section VII).

Series D-2: Double Seal Parallel Fiber

The construction of Series D-2 hollow fiber modules is indicated in Design 2 of Figure 2. A potential advantage of this design is the more streamlined shell-side flow afforded by the elimination of fiber loops, and the ready provision for reversal of feed flow. Assembly is similar to that employed for Series D units, except that tubesheet seals are formed at both ends of the bundle (thus, no looped fibers remain) and feed/brine ports are cast into the tubesheets. As indicated in Figure 2, inclusion of a side entry port in the middle of the pressure vessel permits operation in three different modes. In all modes, product water is removed simultaneously from both ends of the unit. Design details for Module Number D0013-2 are given in Table 13.

TABLE 12

Specifications for Hollow Fiber Module D009

(Test conditions: 3000 mg/l NaCl feed at 250 psi, 50% recovery, 70° F)

Hollow Fibers:	
Dimensions, OD/ID, microns	300/100
Number of fiber ends	16,000
Fiber type	40:60 CA, 88° C
Packing density	0.65
Active fiber area, ft^2	70
Pressure Vessel:	
Construction	316 stainless steel
Length, in.	18
Inside diameter, in.*	1.85
Performance Under Test Conditions:	
Product water flux, gfd	3.0
Rejection, %	90
Productivity, gpd	200
Shell-side pressure drop, psi	5
Bore-side pressure drop, psi	15

* Pressure vessel is nominal 2" pipe. Dimension given is that for an insertable PVC liner encasing the fiber bundle.

TABLE 13

Specifications for Hollow Fiber Module D0013-2

Type: Parallel fiber, with an RTV secondary seal and an epoxy primary seal at each end; hollow fiber bundle fits into metal pressure vessel and is held in position by snap rings; brine-side seal is provided by an O-ring at each end, fitted to a groove in the epoxy tubesheet; multiple brine discharge ports penetrate the tubesheet at each end.

Hollow Fibers: Approximately 16,000; 300 micron OD, 100 micron ID; 40:60 cellulose acetate; packing factor 50%.

Module Dimensions: 2.072" ID; 56" in length; total membrane area 227 ft^2.

Operation: Feed enters pressure vessel through an inlet port situated at midpoint; brine and product water discharge at both ends. Alternate operation is feed through one of the multiple tubesheet ports, brine discharge at the other, and collection of product water at both ends. A third operational mode involves feed through both ends with discharge through the center port.

Performance: Approximately 500 gpd product water capacity with 90% rejection of 1500 mg/l NaCl feed at 250 psi and 70° F. Initial laboratory data (3000 mg/l NaCl, 250 psi, 45% recovery, fed at one end, discharged at other): 1.84 gfd overall flux; 92% rejection at feed end, 88% at reject end; 2.21 gfd and 90%/90% at 300 psi. Approximate shell-side and bore-side pressure losses under cited laboratory test conditions at 250 psi are 15 and 22 psi, respectively.

An extensive laboratory investigation of Module D0013-2 was also completed. Measurements of flux and rejection were made as functions of pressure, feed salinity, and recovery. The flux provided by the module, about 2 gfd at 250 psi, or about 500 gpd, was less than expected. Otherwise, however, performance under a variety of test conditions was quite satisfactory. The three operational modes were examined in the laboratory: co-current, with shell-side feed introduced at the center of the cylindrical pressure vessel, brine discharge and product water discharge from each end; counter-current, with feed introduced at each end and brine discharged from the center; unidirectional, with feed introduced at one end and brine discharged at the other (center port inoperative). The latter mode is co-current with respect to approximately half the fiber bundle length and counter-current with respect to the remaining length. Because of shell-side pressure drops and progressive increase in steady-state salt concentration along the length of the bundle during normal operation at recovery, this mode necessarily provides a different flux and rejection (water quality) at one end of the module than at the other. Different product water concentration levels at opposite ends of the unit were, in fact, observed in the lab checks with unidirectional flow.

Laboratory results for unidirectional flow, with combination of product and brine streams, may be summarized as follows:

(a) Flux was linear with pressure up to 300 psi, using water, 3000 mg/l, and 5000 mg/l NaCl feeds. Intercepts on the pressure axis approximated the osmotic pressures of the feeds.

(b) Rejection of NaCl increased with increasing pressure, appearing to level off at about 90%. An asymptote less than 100%, according to the solution-diffusion model,[4] would result from leaks (through which contributions to both salt and water flux are pressure dependent). In our case, it is quite likely that slight leakage past the O-ring pressure seals contributed.

(c) Flux as a function of recovery, from 10% to 80%, passed through a shallow maximum. This result is quite reasonable and is attributable to decreased average shell-side pressure (at low recovery, where pressure loss is significant) and to decreased driving pressure (large osmotic pressure contributions at high recovery).

(d) Process rejection as a function of recovery, determined from product and feed concentration, decreased with increasing recovery. Correction of process rejection for average, local salt concentration and for normal decrease accompanying decrease in flux, yielded a fairly constant "intrinsic" rejection of about 90% for the entire recovery range 20% to 80%.

Following the lab checks, Module D0013-2 was readied for field service at the Chapel Hill field installation (cf. Section VII).

Series R: Radial Flow

As illustrated by Design 3 of Figure 2, the radial flow arrangement involves feeding a pressurized stream through the center of a hollow fiber bundle by means of a porous feed tube. Potential advantages in waste water treatment appeared to be superior flux and rejection available through minimization of flow channeling. Feed flows radially outward, through the bundle, collecting at the outer surface of the bundle and discharging through a port located midway along the pressure vessel.

As with Designs 1 and 2, assembly of the radial-flow hollow fiber bundle entails winding the hollow fiber yarn onto a mandrel to form a parallel array of hollow fibers. In this design, however, the winding is done about the porous feed tube, which therefore becomes a permanent part of the assembly. RTV and epoxy seals are formed at both ends (a single seal, looped fiber arrangement is an alternate design). The fiber bundle may be consolidated at intermediate stages of the winding by wrapping it with a porous fabric. The fabric also becomes a permanent part of the unit.

Several radial-flow modoules of 200-500 gpd capacity were constructed[5] during the course of this program and one was specifically evaluated for use in waste water service. Laboratory performance was quite satisfactory. On the recommendation of EPA personnel, however, who had experienced severe fouling problems with this design, no radial-flow units were actually operated with secondary municipal effluent. Instead, efforts were directed to more promising designs.

Series W: Woven Fabric

The final hollow fiber concept evaluated in this program was the woven fabric, Design 4 in Figure 2. Our objective in considering this arrangement was to construct a module more resistant to fouling by decreasing the fiber density and enlarging the water passages throughout the fiber bundle. The method involved weaving a fabric on a hand loom, using cotton twine as warp filaments, and hollow fiber yarn as fill material. When rolled and assembled into a working module, the hollow fibers end up running axially and parallel, as in the D-Series design (Design 1, Figure 2), but spaced and positioned by the (inert) warp filaments running circumferentially through the bundle.

Initial work involved evaluation of weaving parameters and materials and testing of small fabric samples under reverse osmosis conditions. On the basis of the preliminary work, detailed design parameters for a demonstration module (WA series) were specified. These are summarized in Table 14 and Figure 3. Module components required are given in Table 15. The cotton warp element was selected primarily for convenience; nylon or other synthetic filaments of appropriate characteristics would be more suitable for long-term waste water service.

Two 4" x 6" test samples of hollow fiber fabric were loosely rolled, potted in epoxy, and assembled for standard evaluation of reverse osmosis properties on our test board. Figure 4A shows one such test sample. Initial performance of both was very good: 4.8 gfd with 93.2% rejection and 5.2 gfd with 95.4% rejection, under test with 3000 mg/l NaCl feed at 250 psi and zero recovery. Performance on both samples subsequently declined, but this was believed due to kinking of the (unsupported) fabric. As the latter problem would not arise in WA series modules, we interpreted the test board results as evidence that fabric preparation does not harm the hollow fibers and that the design proposed should therefore be practicable.

Work next proceeded on preparation of the five-foot length of fabric for demonstration module WA001. Weaving was done on a hand loom, using a manually inserted shuttle. The 50:50 acetone:formamide fiber was employed. To keep the fibers wet, it proved simplest to submerge the entire loom in a shallow pan and weave the fabric under water. Weaving time per one-foot length of full-width fabric was approximately 2 1/2 hours. (The process could, of course, be automated and vastly

TABLE 14

Design Parameters for WA Series Hollow Fiber Modules

General Description: A reverse osmosis unit with a woven fabric fiber bundle incorporating cellulose acetate hollow fibers aligned for axial shell-side flow; looped fiber configuration with single end seal; stainless steel hardware.

Hollow Fibers: Standard 40:60 cellulose acetate, 300 micron OD, 100 micron ID, zero-length flux of 4 gfd with 97% rejection of 3000 mg/l NaCl at 250 psi and zero recovery; pressure capability to 300 psi. Alternate fiber is 50:50 cellulose acetate, 300 micron OD, 100 micron ID, zero length flux of 3 gfd with 97% rejection.

Fiber Bundle: Incorporates a 5-foot length of annealed, 15-inch width fabric involving closely packed, five-filament hollow fiber fill yarn woven with 30 mil diameter soft cotton twine warp spaced at 0.2-inch intervals. Fabric thickness in single layers is approximately 70 mils; in wound layers, approximately 45 mils. The (experimentally observed) fiber count is such that 85 feet of single filament hollow fiber is consumed per inch fabric width per foot fabric length. The fabric is wound on a solid nylon mandrel such that the hollow fibers are co-axial with the mandrel, overlaid with a protective wrap, and sealed to the mandrel with an RTV dam at one end. Protruding, looped fibers at this end are sealed in an epoxy tubesheet and cut to provide the product water outlet. Of the 15-inch fabric width (bundle length), 3 inches is allotted for both seals and end trimming, leaving an active length of 12 inches. Fabric as woven is prepared on a 16-inch loom (as-woven width is 15 1/2 inches), allowing for shrinkage of 1/2-inch on annealing. Total active fiber area is 16.6 ft^2.

Pressure Vessel: Nominal 2" stainless steel pipe fitted with a tapped threaded pipe cap at the brine discharge end, a pipe nipple enclosing the bundle tubesheet, a PVC product water cap, and a Victaulic side entry coupling for the feed stream.

TABLE 14 (continued)
Design Parameters for WA Series Hollow Fiber Modules

Module: Operation is with counter-current, axial shell-side flow. Design productivity is 50 gpd (3.0 gfd) with 95% rejection of 3000 mg/l NaCl at 250 psi and 50% recovery. Bore-side pressure drop under test conditions is approximately 30 psi; shell-side pressure drop is small. Local fiber packing density (within fabric bundle) is approximately 0.26; module area utilization is about 1000 ft^2 of membrane per ft^3 of active pressure vessel.

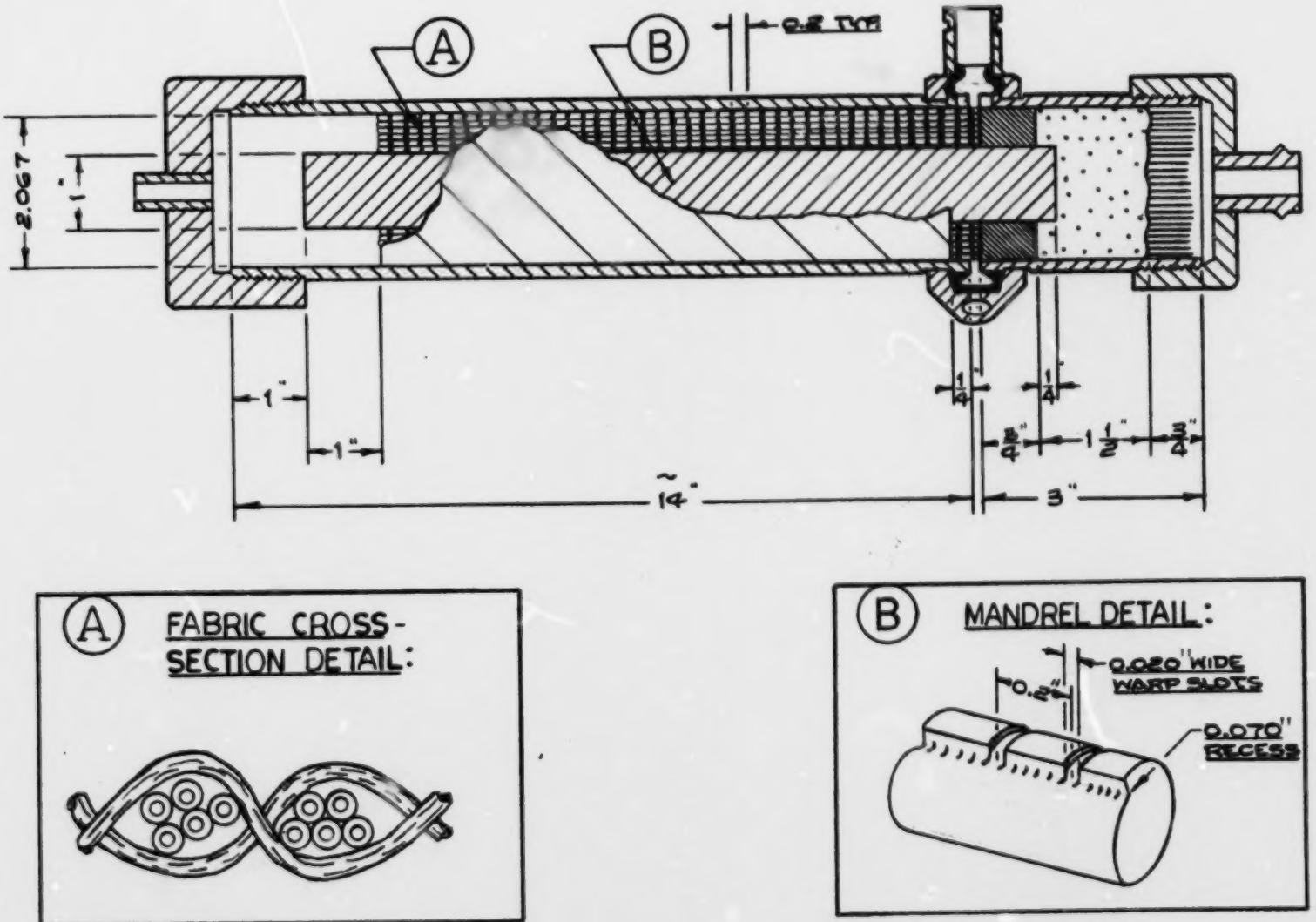

Figure 3. Engineering design of WA Series hollow fiber module

TABLE 15

List of Materials for WA Series Hollow Fiber Module

Item	Quantity	Description
Hollow fiber	1320 ft	As-spun, 5-filament hollow CA fiber yarn
Warp fiber	410 ft	30 mil diameter soft cotton twine
RTV	2 oz	Secondary seal
Epoxy	5 oz	Tubesheet seal
Pressure vessel	1	Nominal 2" (2.067" ID) 316 stainless pipe, 14" length, one Victaulic grooved, one-threaded end
Tubesheet nipple	1	Nominal 2" stainless pipe, 3" length, one Victaulic grooved, one-threaded end
Brine discharge seal	1	2" 316 stainless pipe cap, drilled and tapped for brine discharge tube
Coupling	1	2" side-entry Victaulic coupling, Style 72
Product water cap	1	2" PVC threaded cap, drilled for product discharge tube
Bundle mandrel	1	1" diameter nylon rod, 14" length
Cartridge liner		4' length of 2" wide Cerex® spun-bonded fabric, 6 mils thickness
Discharge port fittings	2	Brine discharge pipe and product water pipe, sized to suit test facility

(C) fabric for demonstration module, rolled and ready for annealing

(B) 15" x 60" fabric for demonstration module

(A) 4" x 6" rolled fabric test sample

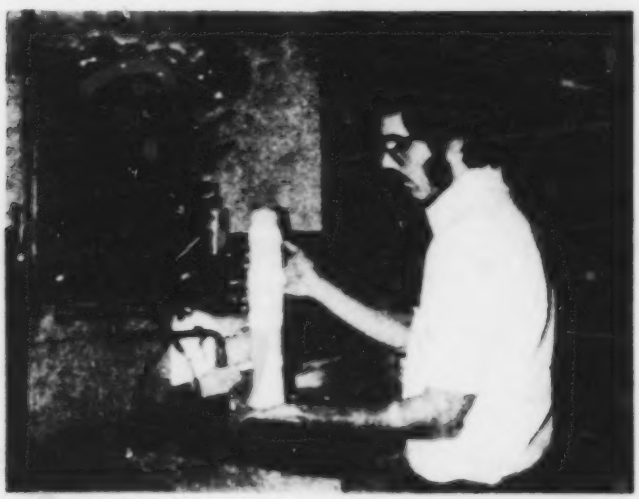

Figure 4. Construction of woven fabric hollow fiber modules

accelerated.) A section of the first five-foot fabric sample is shown in Figure 4B. The loosely rolled bundle, ready for hot water annealing, is shown in Figure 4C.

Assembly of the module involved attaching and rolling the annealed fabric onto a mandrel and, at the same time, forming a 3/4" seal of RTV cementing the fabric roll to the mandrel. A final wrap of Cerex consolidates the bundle. End-treatment, gelatinization, end-drying, and potting of the tubesheet proceeded as with conventional looped fiber designs. (The warp strings were removed from the tubesheet end prior to potting.)

Module WA001 was assembled with its pressure vessel and laboratory tested. Results of the laboratory check are compiled in Table 16. They were very satisfactory, and within performance specifications for this hollow fiber. A photograph of the assembled module, ready for field testing, is shown in Figure 5.

TABLE 16

Laboratory Reverse Osmosis Performance for Hollow Fiber Fabric Module WA001

(3000 mg/l NaCl feed at 70°F)
50:50 A:F CA fiber

Test Day	Pressure psi	Recovery %	Flux gfd	Productivity gpd	Rejection %
1	135	20	0.81	14	93.6
2	125	20	1.0	18	93.3
2	205	20	2.0	33	95.1
2	250	20	2.6	43	96.3

Following the successful construction of woven fabric Module WA001, and its subsequent excellent performance in field service (see Section VII), a second unit, WA002, was constructed. Design specifications were identical with those for the first unit, except that

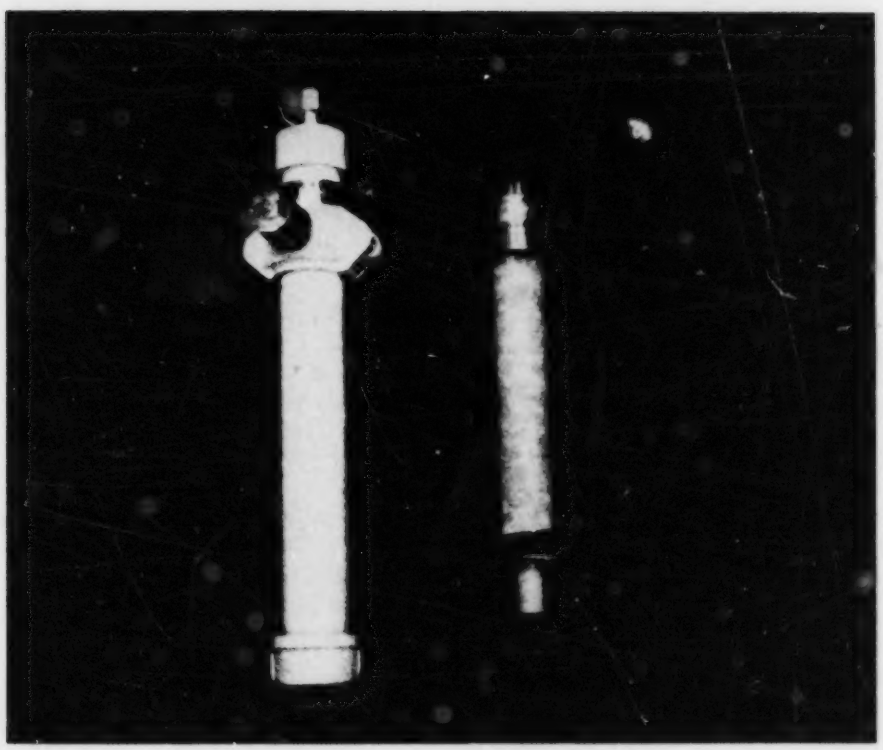

Figure 5. Photograph of woven fabric module WA001

WA002 was assembled with the 40:60 cellulose acetate fibers used in all other modules examined in this program and, as a result of using different equipment, fiber count increased from 85 to 105 feet of single filament per inch-foot. Assembly of WA002 was done on a slightly more sophisticated loom, with foot operated heddle and manual shuttle, shown in Figure 6. Total active fiber area was 17.7 ft^2. Laboratory performance is recorded in Table 17.

Evaluation of the woven fabric concept completed our investigation of hollow fiber module designs. It was apparent from all data collected that this design was the most successful in waste water service. Minimization of dead volume occupied by the center mandrel, substantial improvements in efficiency of fabric weaving, and module scale-up to large diameters were all deemed feasible.

TABLE 17

Laboratory Reverse Osmosis Performance for Hollow Fiber Fabric Module WA002

(4400 mg/l NaCl feed at 70° F)

Test Day	Pressure psi	Recovery %	Flux gfd	Productivity gpd	Rejection %
1	250	40	4.9	87	87
2	250	13	4.3	76	93
2	250	35	4.3	76	90
2	300	23	5.2	92	92
3	250	20	4.0	71	92

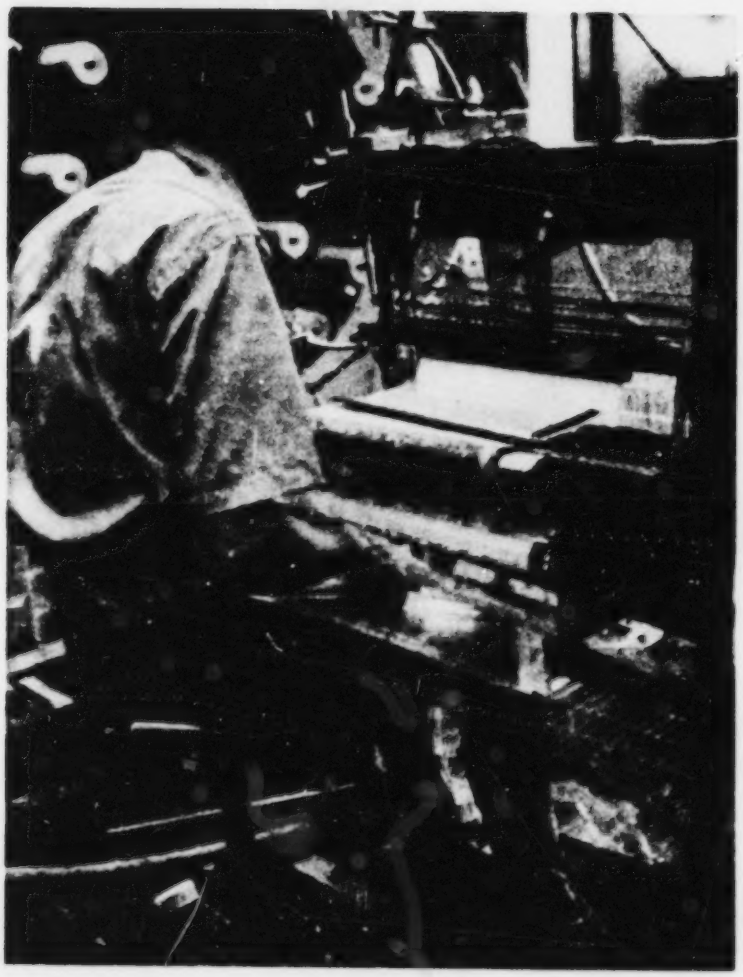

Figure 6. Le Clerc, Medica Model 22-4 loom used in assembly of Module WA002

VI INVESTIGATIONS OF MODULE FOULING

Laboratory Performance with Surface-Active Agents

To examine more closely the results which had been obtained on the small test loop, some of the work conducted before was repeated with a full-size, D-series module, D008. This work was considered the more important because test loop results had not indicated an effect as pronounced as it was with flat membranes. The discrepancy had been particularly noticeable with the cationic surface-active agent, benzalkonium chloride. Therefore, new experiments were performed with a solution which contained approximately 500 mg/l of dissolved Hyamine 3500 ® (Rohm and Haas). This product is an alkylbenzyl-dimethylammonium chloride, in which the alkyl group is in the range 10-16 carbon atoms long.

The apparatus used for this test was similar in principle to the small test loop, but considerably larger; liquid pumping was performed by a Goulds multi-stage centrifugal pump which operated at 3430 rpm. Its output was sufficiently large that a substantial part of the circulated liquid stream had to be by-passed, rather than sent through the module if measurements were to be made at a reasonably high recovery. The system operated as a closed loop; except for samples removed, all circulated liquid was returned to the starting bath.

Results obtained with the benzalkonium chloride are indicated in Table 18. Basically, they show that there is a slight, but definite fall-off in flux with time which takes place mainly in the early stages. The effect, however, is considerably less pronounced than it is with flat membranes.

A second test was performed with this solute under modified conditions, the whole test being conducted at constant pressure (250 psi) and flux being measured at fixed time intervals. Since previous work had indicated that the greatest effect took place in the early stages of operation, this test was run only for a few hours. In this case, temperature-corrected fluxes showed only a slight change with time, as shown in Table 19. This was not only slight, but indecisive as well. It was concluded that this particular solute, per se, caused no specific fouling effect of appreciable magnitude.

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TABLE 18

Performance of Hollow Fiber Module D008 with Benzalkonium Chloride Solutions

Pressure, psi	Flux, gfd	Flux/pressure	Rejection, %
100	1.49	0.0149	98.6
150	2.08	0.0136	95.8
200	2.79	0.01395	95.0
250	3.32	0.0134	97.0
300	3.92	0.01306	97.2
300 (1 hr later)	3.92	0.01306	97.0

TABLE 19

Flux-Time Relationship with Benzalkonium Chloride Feed at 250 psi

Time (hr)	Flux, gfd, corrected for temperature
Start	3.91
0.67	4.08
1.67	4.08
2.67	3.77

An effort was then made to determine whether such an effect was demonstrable for an anionic surface-active agent (sodium alkylaryl-sulfonate). In this case, severe foaming was observed in experimental work using a 500 mg/l solution, but, once more, the results were of such a nature as to suggest that no significant effect was operative. Data are given in Table 20.

TABLE 20

Flux-Time Relationship with Sodium Alkyl-Arylsulfonate Feed at 250 psi

Time (hr)	Flux, gfd, corrected for temperature
Start	3.83
0.5	3.10
1.5	4.28
2.5	4.18

These results prompted us to make a theoretical study of the probable effects to be expected in hollow fiber systems. From analysis of flow behavior in such systems, it became clear that polarization phenomena are usually much less important in hollow filament systems than they are with flat membranes. Thus, the build-up of a "secondary membrane," consisting of a layer of the fouling solute, is far less likely to occur in hollow filament systems, and our failure to observe a very pronounced effect was a predictable result.

Laboratory Simulation of Fouling

Gelatin was adopted as a typical fouling water component because it is representative of a class of materials which may well be found in waste waters--partially degraded proteins. Tests with this solute were performed with a D-series module (D008), using the same test loop mentioned above. Fouling was caused by adding a gelatin solution to a sodium chloride solution which was already being circulated. Results obtained are indicated in Table 21; it is interesting to note that no great effect was observed at the 1000 mg/l level, but that a very

TABLE 21

Analysis of Flow Data for Module D008

Investigation: Intentional fouling of a 2", standard looped fiber unit, 65% packing density. Experiment involved: (1) test with water/NaCl; (2) foul with gelatin/NaCl; (3) flush with water/NaCl; (4) flush with Biz®; (5) check with water/NaCl. All tests were with 1000 mg/l NaCl at 250 psi and 21° C. Gelatin feed concentration was 1000-2000 mg/l.

1	2	3	4	5	6	7
Condition	% Recovery	gfd Flux	% Rejection	mg/l in product	mg/l, corrected for recovery	mg/l, corrected for flux
(1)	8	3.70	88	119	114	114
	48	3.70	79	210	141	141
(2)	47	3.31	85	146	101	94
	64	2.34	63	370	198	125
	53	1.88	72	280	178	90
	53	1.75	70	300	191	90
	42	1.13	34	650	478	146
(3)	37	0.69	11	860	666	124
	7	0.71	37	610	590	113
(4)	Biz flush					
(5)	45	3.48	82	182	130	122

TABLE 21 (continued)
Analysis of Flow Data for Module D0008

Column 6	Corrected mg/l is observed mg/l times $2/(1 + 1/(1-R))$, where R is decimal recovery. (Correction assumes a linear increase in axial salt concentration from feed end to reject end.)
Column 7	Corrected mg/l is Column 6 value times observed flux, divided by reference flux (3.70).

pronounced fouling effect was observed at the 2000 mg/l level. Moreover, this effect increased with time. Also, this fouling was evidently not readily removed by simple replacement of the gelatin solution with tap water. On the other hand, the fouling was removed very efficiently by treating the module with a Biz® solution which had been adjusted to approximately pH 7. (Biz is an enzyme-detergent product manufactured by the Procter & Gamble Company. Use of this product does not constitute an endorsement or recommendation.)

These results confirm that fouling with purely proteinaceous matter can be readily removed by treatment with suitable cleaning agents, particularly those which contain enzymes, and should not represent a serious long-term problem.

Analysis of Fouling in Field Service

In contrast to laboratory results, fouling of experimental modules in field service showed quite another pattern in operation on secondary effluent from the University of North Carolina Wastewater Research Center, a pilot plant installation. It should be emphasized that all secondary effluent processed had been filtered before circulation through the modules; this filtration was made increasingly thorough with the passage of time, as it became apparent that a severe fouling problem was present. Initially, an opportunity was provided for some settling to take place in the supply water; and, after settling, the water was passed through a 50-micron Cuno filter. It soon became apparent that little real settling was taking place, and the settling tanks were replaced with a sand filter (Swimquip Model FRP-20, 20" diameter, high-rate sand filter, designed primarily for swimming pools), while still retaining the 50-micron cartridge filter. Subsequently, a 5-micron filter was placed in line with the 50-micron filter, as well.

In spite of the efforts made to ensure thorough removal of suspended material, operation of all modules except the W series was characterized by a steady drop in product water flux which could be only partially restored by systematic Biz treatments. In all cases, we ultimately found it necessary to remove the module from service and subject it to a radical cleaning treatment, which consisted of completely removing the hollow filaments from the housing and physically removing the fouling material. A portion of this material was greasy in nature. It may have resulted either from

oil leakage in the pumping system of the Wastewater Research Center (a known occurrence), from incomplete degradation of animal or vegetable fat in the primary and secondary treatment stages, from other hydrocarbon oil present in the wastewater, or from a combination of some of these. Since repeated Biz treatments seemed to have been relatively ineffective in removing it, we believe that hydrocarbon oils probably account for much of the trouble.

The greasy component of the fouling material, however, was only a relatively minor part of the whole mass. The greater part of it consisted of a solid substance, part of which was amorphous and evidently organic, and the remainder of which was a roughly crystalline solid, light brown in color, which appeared to be inorganic. Several sets of analyses were performed on this solid, both in our own laboratories and by personnel of the Robert A. Taft Water Research Center, Cincinnati, Ohio. These invariably showed a high content of inorganic substances (residue on ashing)--usually in the range 67-75%. However, the analyses by the Robert A. Taft Water Research Center personnel also showed a fairly high chemical oxygen demand, which is presumably attributed to the organic components of the solid. The nature of the inorganic component has not been ascertained. Quantitative analysis has shown that the major cation is calcium (16.6%). Emission spectroscopy showed the presence of a number of other metals, but not in large amount (Fe, 0.7%; Mn, 0.2%; Na, 0.2%). Analysis for CO_2 showed only 0.5% in the original sample, or 1.8% in the ash. (Calcium carbonate requires 45.5%.) Similarly, only 1.18% sulfur was found present (much too low for calcium sulfate). However, a phosphorus content of approximately 15.4% was determined. This is too low for tricalcium phosphate (20.0%), which might not be stable under the prevailing pH conditions in any case (pH 6.8). It is also too low for $CaHPO_4$, which is a conceivable constituent (P, 22.8%). The calcium analysis is about right for $Ca(H_2PO_4)_2$ (Ca, 17.1%), but this substance is moderately water-soluble, and would not be expected to accumulate in the module, even under conditions of extreme polarization. Moreover, the phosphorus analysis is too low (theory for calcium superphosphate, 26.5%). The atomic ratio of phosphorus to calcium is apparently close to 1:1 (actually, 5:4). This rules out the assignment of this material as hydroxyapatite, $Ca_5(OH)(PO_4)_3$, which had been suggested by some of the personnel at the University of North Carolina Wastewater Research Center. Possibly analysis

of carefully extracted solid, containing only the inorganic portion, will be more fruitful.

Attempts to minimize or eliminate this organic or inorganic fouling by regular and systematic cleanings with Biz were largely unsuccessful. Controlled chlorination of the feed and adjustment of its pH to 5.5 also proved ineffective. For some reason, modules of the W design appeared to be much less subject to this type of fouling; the reason for this difference is not known with certainty, but it appears that it must be related to the uniform, consistent flow profile which is maintained in such modules, with very limited opportunity for stagnant regions of high local supersaturation to develop.

There is no reason to assume that the particular design used in this demonstration module is optimum. Further work along the lines suggested by it is strongly indicated. Work should include designs providing for higher overall productivity, as well as even more uniform flow characteristics.

When we first became aware of the fouling problem in field work, our initial assumption was that fouling was the result of bacterial multiplication in the module and connecting lines. To some extent, this was probably true. In efforts to eliminate or control fouling from this cause, we adopted measures which should have eliminated bacterial growth. First, a simple chlorinator of the type used to treat home swimming pools was installed. This was a cartridge which contained large lumps of trichlorotriazinetrione (trichloroisocyanuric acid). It was installed in such a way that it constituted a by-pass loop in parallel with the sand filter, so that the pressure drop across the filter created a driving force to move liquid through the chlorinator. Flow was then throttled with a simple needle valve, in such a way that the chlorine content of the feed water was adjusted to 0.5-2.0 mg/l, as determined with a chlorine test kit.

While this treatment undoubtedly did some good in reducing bacterial multiplication, it did not solve the basic difficulty. Module fouling continued at about the same rate, as judged by the rate of flux decline with time.

Attention was then turned to pH adjustment, to see if a different pH would help prevent the deposition of inorganic solids. Cellulose acetate hollow filaments can be used down to a pH of about 4.0, but this pH is at the threshold of polymer degradation, so a pH of 5-5.5 was sought. An experimental titration of the feed water showed that it had an appreciable buffering capacity, so that a definite feed of acid was required to reduce the original pH (6.8) to the desired level. In practice, we settled upon a system in which 0.5 molar sulfuric acid was fed into the feed water line from a large reservoir by using a perisaltic pump which operated continuously, at a delivery rate of 3.5-4.0 ml/min. The rate of water flow through the system at the time was approximately 2100-2150 ml/min. This system proved somewhat less effective than we had hoped, since the Tygon capillary bore tubing used in the pump hardened with use and sometimes failed to deliver acid. At about this time we discovered that the chlorination system itself was reducing the pH of the feed water to about 5.5, and therefore there was no real need to continue with the acid feed.

The use of the acid pretreatment did not seem to affect the rate of fouling greatly, either. While no measure adopted ever fully solved the fouling problem, the best set of conditions which we were able to work out included the following procedures: (1) thorough filtration of the feed water (sand filter, followed successively by a 50-micron Cuno filter and a 5-micron Cuno filter; (2) relatively high liquid flow rate through the system, to minimize opportunity for purely physical fouling; (3) chlorination; and (4) acid treatment. These measures were supplemented, of course, by regular Biz cleanings (at least once a week, sometimes twice), regular change of filter cartridges, and systematic backwashing of the sand filter (daily). Only the woven fabric module did not require Biz treatment.

Typical performance characteristics of the various modules with respect to fouling, as indicated by flux-time variation, are shown in Figures 9A-13A of the following Section VII. These show quite graphically, the type of behavior which was characteristic of both single-ended and double-ended modules; Figure 13A shows the performance of the woven fabric module tested; the improved flux stability with time is apparent.

Fouling by inorganic solids appeared to be the greatest single factor in causing decline in module efficiency. Such accepted measures as careful filtration, Biz treatment, chlorination, and pH adjustment had only limited effect Thus, one may conclude that such factors as bacterial multiplication, slime deposition, etc., were not decisive in this particular operation. On the other hand, deposition of solids whose formation was not affected by these procedures appeared to take place steadily, ultimately requiring removal of the module for thorough clean-up. For the most part, these solids appeared to be inorganic.

VII FIELD RESULTS

Field Test Facilities

The wastewater used in our experimental work was taken from the pond into which secondary effluent from the University of North Carolina Research Center trickling filter ran, by simply tapping off from a line which supplied such water for test purposes. Over the period during which we determined content of various substances in the feed stream (filtered) to our module, the mean contents of certain key solutes were as shown in Table 22.

As noted previously, the pH of the feed water used in this work was about 6.8. The water itself did not normally contain visible suspended particles; nevertheless, it had a distinct grayish opalescence which was due to very finely divided suspended particulate matter characteristic of trickling filter effluent. In early work with the sand filter, turbidity measurements were used to establish the frequency requirements for backwashing; turbidity of the sand filtered effluent equal to about 15 Jackson Turbidity Units (JtU) was considered marginally satisfactory. This value was reached in 1-2 days after each backwashing operation.

In spite of the fact that visible suspended solids were normally not present in the secondary effluent, deposition of black solid matter began to take place in the connecting lines very soon after start-up, and this was particularly noted near the 50-micron filter. It was normally necessary to replace the cartridge in this filter at least once per week, sometimes more often--otherwise pump starvation began to take place. Moreover, during the period when settling tanks were being used, the formation of floating solid material in these was quite evident. Initially this was assumed to be due to bacterial growth; however, it seems very likely that a part of it was also due to simple agglomeration of finely divided solids present in the water. This phenomenon was one of the reasons for eliminating the settling tanks; the principal other reason being that no great amount of settling ever appeared to take place in any case.

TABLE 22

Content of Certain Solutes in Filtered Secondary Effluent
University of North Carolina Wastewater Research Center

Solute	No. of Observations	Content, mg/l
BOD_5	47	35-36
Kjeldahl nitrogen	42	20-21
Na^+	54	35-36
Cl^-	56	36-37
Organic carbon	22	48-49
Inorganic carbon	22	33-34
Phosphate (total)	17	6-7
NO_2^-	*	ca. 0.01
NO_3^-	**	ca. 0.1

* Usually not even reported.
** Data extremely limited. Occasionally ran as high as 1.1 mg/l.

The test assembly which was used in evaluating module performance is shown in Figures 7 and 8. It was originally designed to provide for operation of two modules simultaneously. Except for a brief period when both module D009 and module D0013-2 were operating, the entire pump flow was routed into a single module.

Secondary effluent was taken from one of the final clarifiers of the Wastewater Research Center by tapping on to a supply line already in existence.

The test assembly did not operate as a closed loop in the ordinary sense. Water was taken from the clarifier, processed through the test unit, and continuously returned to the reservoir (both product water and brine), samples being withdrawn only as needed. The solute content of the clarifier reservoir changed continuously,

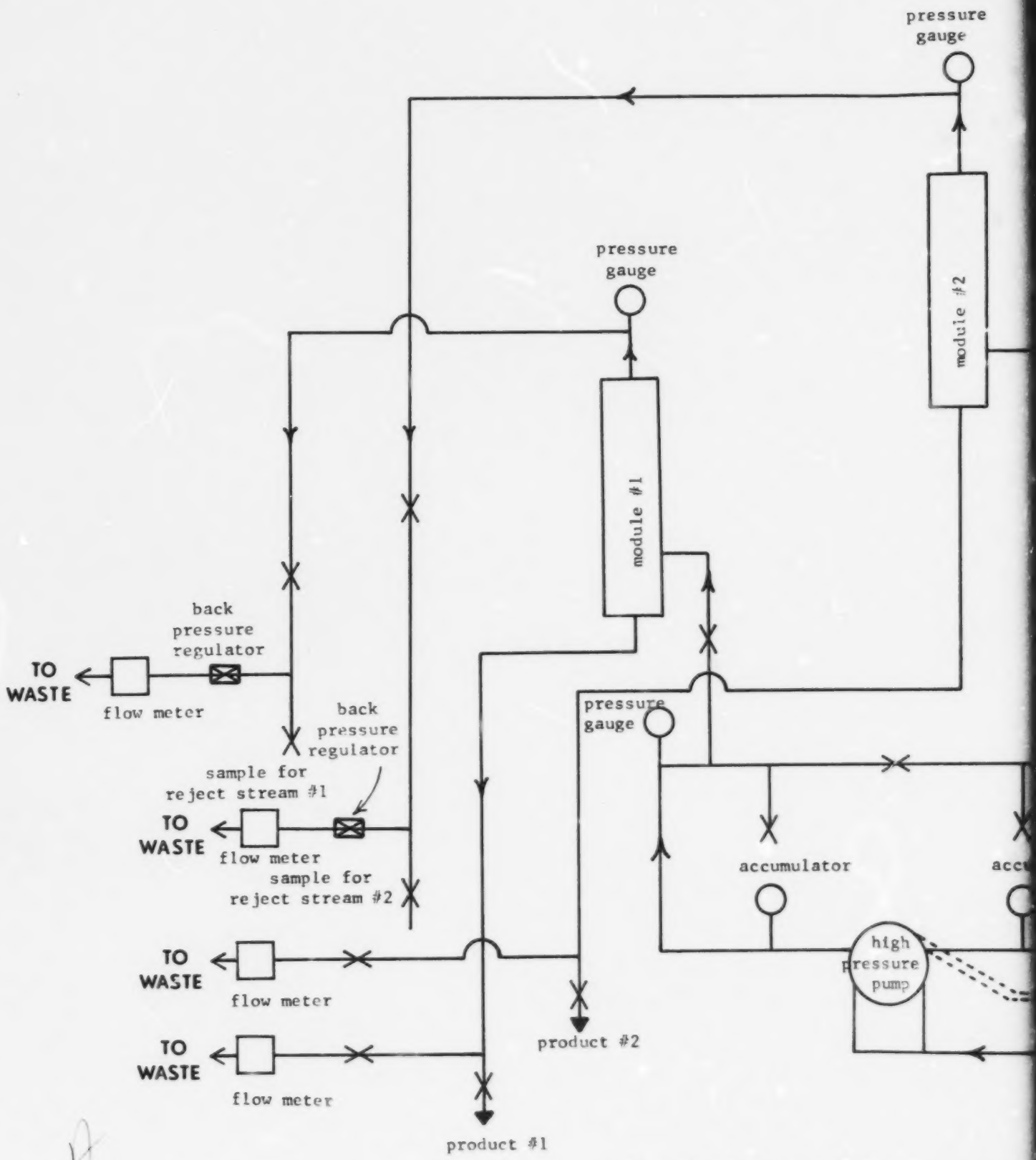
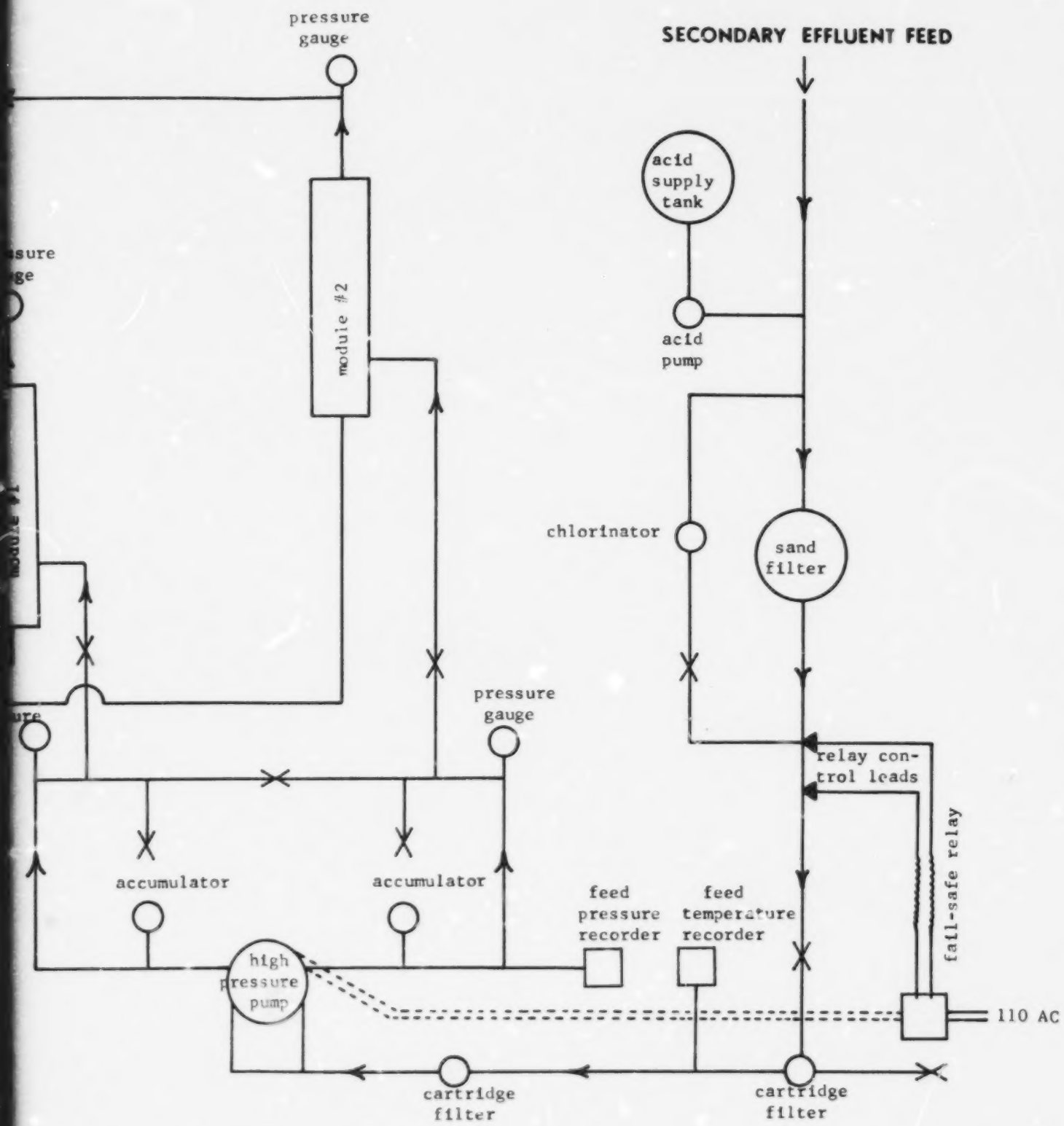
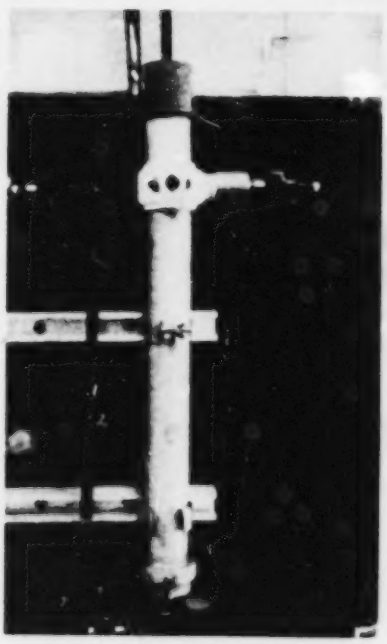


Figure 7. Schematic of field reverse osm



ure 7. Schematic of field reverse osmosis test loop for hollow fiber units



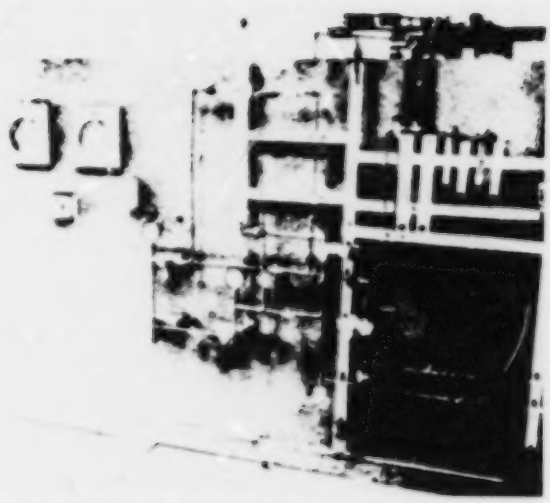


Figure 8. Field unit for testing of hollow fiber modules with secondary municipal effluent

owing to influx of water from the trickling filter and discharge of overflow into nearby Morgan Creek.

Reference has already been made to settling tanks which had been originally installed in the feed water line; these are not shown in the schematic sketch of Figure 7, since they were removed at an early date. The idea behind them was that, since particulate matter occurs in the feed water (although almost colloidally divided), it should be possible to remove at least part of it by settling. When they were in use, the procedure was as follows: supply water entered a 200-gallon polyethylene tank via a simple valve which was opened and closed by a float; this provided a fairly constant water level near the top of the tank. A connecting line was provided from this tank to a second one, passing through a wide-bore solenoid valve which was controlled by a simple clock motor and adjustable cam operating against a microswitch. The "on" period of the microswitch was so adjusted that the second tank never became completely empty. Feed for the test system was taken from a point somewhat above the bottom of the second tank. In operation, this system proved unwieldy and ineffective; no great amount of settling appeared to take place, but much floating insoluble matter was soon seen. This may have been either a product of bacterial multiplication (which was known to occur to some extent within the lines) or a product of simple agglomeration of particulate matter already present. In any case, the size and complexity of this portion of the assembly was steadily reduced, and it was finally eliminated altogether.

The bacterial multiplication alluded to above was evidenced by the development of a foul odor in the water from the module test system at points where there was any opportunity at all for stagnation. There was also evidence of gas pressure development; in early operation this pressure had to be bled off regularly. Later on, means were found to combat it; the most effective ones seemed to be relatively high liquid velocity through the system (operation at low recovery), and chlorination of the feed. The effect of a pH change was less conclusive, but may have contributed to reducing the severity of this problem. It is to be noted that these measures were relatively effective against anaerobic bacterial multiplication, but were far less effective against the fouling problem which has been mentioned above.

A summary of field experience with hollow fiber modules of three designs is given below. Design specifications and laboratory performance for each were described in Section V. Unless otherwise noted, field operating pressure was 250 psig and all flux data are corrected to 70° F. Graphical records of field results are contained in the set of Figures 9A through 13E.

Series D Modules

Module D009: The first module tested was of the single-end type, previously described, incorporating parallel, looped fibers within a housing. This module was installed on 2 March 1971, and was operated over a period of 108 days, including a total of some 3.5 weeks down-time for cleaning. In its initial running period of 29 days, its performance was characterized by a steady decline in flux, with brief improvements following each treatment with Biz. Initially these treatments at times gave a higher product flux than was obtained at start-up; however, the response gradually became less significant. Finally, the last two Biz treatments failed to create a very great response at all. During the same period, rejections of key solutes were moderate and tended to fluctuate; it was noticeable that the best results were normally obtained in the period following a Biz flush, but this effect did not persist until the end. It is also interesting to note that the best BOD_5 rejection did not necessarily parallel the best rejection of sodium or chloride ion. The reason for this discrepancy is not known; a possible reason may be that some of the substances responsible for BOD_5 in this system were liquids or gases rather than dissolved solids. Some of these may well display anomalous transmission characteristics through fiber walls. The first cleaning of the module was carried out when flow of brine and product through it had completely stopped. Accumulation of the large amount of solid in fouled modules was first noted at this time.

Upon re-installation, this module performed in a way which fairly closely simulated its earlier performance, even though a sand filter was installed at this time. Again, BOD_5 rejection did not necessarily parallel rejection of sodium or chloride ion. The time required for the flux to drop to a completely unacceptable level was approximately the same as before.

Maintenance of flux level was about the same in the third period of use after cleaning as it had been in the first two periods. Under the conditions of use which were in existence at the Wastewater Research Center, the useful service period before radical cleaning appeared to be somewhere in the range 20 to 30 days. In general, this module appeared to be somewhat less effective in rejecting sodium or chloride ions than was predicted; and the rejection of substances responsible for BOD_5 was erratic, although generally high when the module was in good condition--either freshly cleaned or freshly washed with Biz.

When module D009 was taken apart for the third cleaning, large numbers of opaque white patches were noted among the translucent, shiny hollow filaments. These were quite brittle, and resulted in many broken filaments during handling. Attempts to patch them all were extremely tedious, and an attempt to prepare an intact module of slightly lower throughput by excising them and sealing the ends failed altogether. Otherwise, work would have been continued with this module.

Examination of material from the opaque sections provided little useful information. Microscopic study showed that the hollow filaments in these areas were still intact--the walls were not broken, nor were they collapsed. The material was still soluble in acetone, so it may be concluded that it was not an extensive hydrolysis product of cellulose acetate. Only traces of inorganic material were found present by emission spectroscopy. The opaque areas presented an appearance like that of cellulose acetate which has been precipitated from a solvent into water. A possible explanation is that a physical phenomenon similar to devitrification of glass had occurred. Another is that some product of bacterial origin may have actually caused a partial solution of fibers in these regions, and this cellulose acetate was subsequently "reprecipitated" in a very amorphous form during the removal and cleaning process.

Module D010: This module, also of the single seal, looped fiber design, was installed in service on 10 August 1971 and it was set up from the start with the intention of minimizing the fouling which had been such a problem with module D009. To this end, the water flow rate through the module was greatly increased, and a program

of chlorination was begun. The original objective was to maintain a chlorine level of approximately 2 mg/l in the feed water. In early attempts to adjust this level, a very highly chlorinated stock was obtained; this made BOD_5 determinations meaningless in samples taken at these times. These measures were only partially successful; flux decline with time was almost as severe as it had been before, even though the frequency of Biz treatments was also increased. The principal comment that can be made about results with this module is that BOD_5 rejection appeared to be better than it had been in the first case; this may possibly be due to the chlorination technique, although the analysts adopted a procedure of treating the samples with sodium sulfite to destroy residual chlorine. On the other hand, sodium ion and chloride ion were rejected relatively poorly with this module, and this accounted for the decision to replace it after a considerably shorter period of operation.

Module D008: Installation of this module (on 4 October 1971) was coupled with a revamping of the chlorine feed system, to ensure more reliable and effective operation (a chlorinator of our own design was fabricated, and it was connected in parallel with the sand filter, to utilize the pressure drop across the sand bed to ensure a steady flow of water through the chlorinator cartridge). Moreover, an acid feed was provided, to make sure that the pH of the feed water was maintained at 5 to 5.5. This was accomplished by pumping 0.5 molar sulfuric acid from a large reservoir into the feed line with a small, adjustable peristaltic pump, at a rate of 3.5-4 ml/min. (The feed water proved to have a considerable buffer capacity; otherwise this amount of acid would have been far too great.)

The effect of the added acid was apparently small as compared with the effect of acid liberated from the trichlorotriazinetrione; on several occasions when the pump line was found obstructed, the pH of the treated feed water was not noticeably affected. The manufacturers of this product note that water treated with it normally develops an acid reaction.

On the whole, these measures appear to have helped in maintaining a somewhat higher flux level, or, at least, in slowing down the rate of flux decline. On the whole, also, the overall balance between BOD_5 rejection and rejection of sodium and chloride ions was improved somewhat. However, it should be noted that in each case there was at least one day where the rejection was very poor.

Opportunity was taken with this module to evaluate the possibility of improving module performance by decreasing the filament packing density of fibers in the module. When the module had been operated for two weeks, it was removed, thoroughly cleaned, and reassembled without the liner. This change caused a decrease in filament packing density from 57% to 49%. Results of this test were made difficult to evaluate by the fact that the module sat completely idle for a period of ten days (23 October - 31 October 1971) when the Wastewater Research Center was completely flooded out during a period of exceptionally heavy and prolonged rainfall. However, as nearly as one can estimate, the rate of flux decline and the rejection behavior of the module were not improved; and they may even have been affected somewhat adversely.

Series D-2 Modules

Module D0013-2, representing the double seal, parallel fiber design, was installed on 1 June 1971 and was operated for 44 days. For seventeen days of this period it was operated jointly with module D009; during this period the output capacity of the pump in service was not sufficient to supply each module with water at 250 psig, so module D0013-2 was operated at 150 psig for the first 17 days. When module D009 was shut down, operating pressure was raised to 250 psig. On the whole, D0013-2 appeared to resist decrease in flux due to fouling somewhat more effectively than D009 (looped fiber design), with which it was operating simultaneously. Product flux through it started at a lower gfd level, but never dropped off quite so far as it did with the single-ended module. A portion of this beneficial effect may be the result of the fact that several modes of operation are possible with this module, and each of them was used from time to time. This included the ability to pass feed from one end of the bundle to the other, and to reverse periodically the direction of flow. Such changes may well have had the effect of breaking up the pattern of solids deposition in the module (fouling).

It is difficult to compare accurately the performance of modules D009 and D0013-2 during the period when they were operating simultaneously, because they were operating at different pressures. However, it appears that module D0013-2 was somewhat less effective in rejecting solutes during the time when it operated at 150 psig, and that its performance improved predictably when the pressure was increased. This, of course, is normal for reverse osmosis units.

It was noteworthy that BOD_5 rejection paralleled rejection of sodium and chloride ions more closely in this case.

Module D0013-2 was removed for cleaning on 15 July 1971. In the ordinary course of events it would have been re-installed. Examination of the fiber bundle, however, disclosed the same opaque formations which were present in module D009.

Attempts were made to put this module (and module D009) back into serviceable condition by techniques which have usually been quite successful with cellulose acetate hollow filament modules. First, a systematic effort was made to locate and seal off each broken filament. When feasible, this is easily done by first tying a simple overhand knot in the loose end, then dipping the end into a small amount of "Duco" cement. In actual operation, new broken ends seemed to be generated by handling operations about as fast as the first ones were repaired.

For this reason, a more drastic approach was tried; the opaque areas of embrittled fiber were simply cut out entirely. Then the problem reduced to sealing off the ends of a fairly substantial fiber bundle, all at once. This proved to be very difficult; in spite of repeated efforts, either by dipping into Duco cement or by treating with solvents, some of the ends remained unsealed, as demonstrated by testing with low-pressure nitrogen while the fiber ends were under water.

Series W Modules

The description of this woven fabric module has been given previously. Unit WA001 was installed in service on 17 November 1971, and was operated for 15 days. No change was made in the general parameters of the test board: chlorination, acid feed, and rate of water pumping through this module were maintained just as they had been with the last module used (D008). Since the effective area of the fiber surface in this module was considerably less than in the other modules, its maximum throughput of product was also less, and therefore the percentage of product recovery was quite low. This circumstance may have affected the results obtained in the early phases of work with this module, although later results make this unlikely.

Basically, results with this type of module were extremely satisfying. After an initial period of a few days in which flux declined approximately 25%, flow of product water stabilized at an approximately constant level which did not change significantly over the next week or more. Moreover, rejection of sodium and chloride ions was outstandingly good, never dropping below 85%, even when the percentage of product recovery was increased tenfold. BOD_5 rejection was not so satisfactory; although individual rejections were occasionally quite good, overall performance was only average. During the last three days of use, module WA001 was operated at approximately 65% recovery. Possibly the most interesting fact found here is that rejections did not drop greatly at this increased recovery. In fact, the available data indicate that the BOD_5 rejection improved.

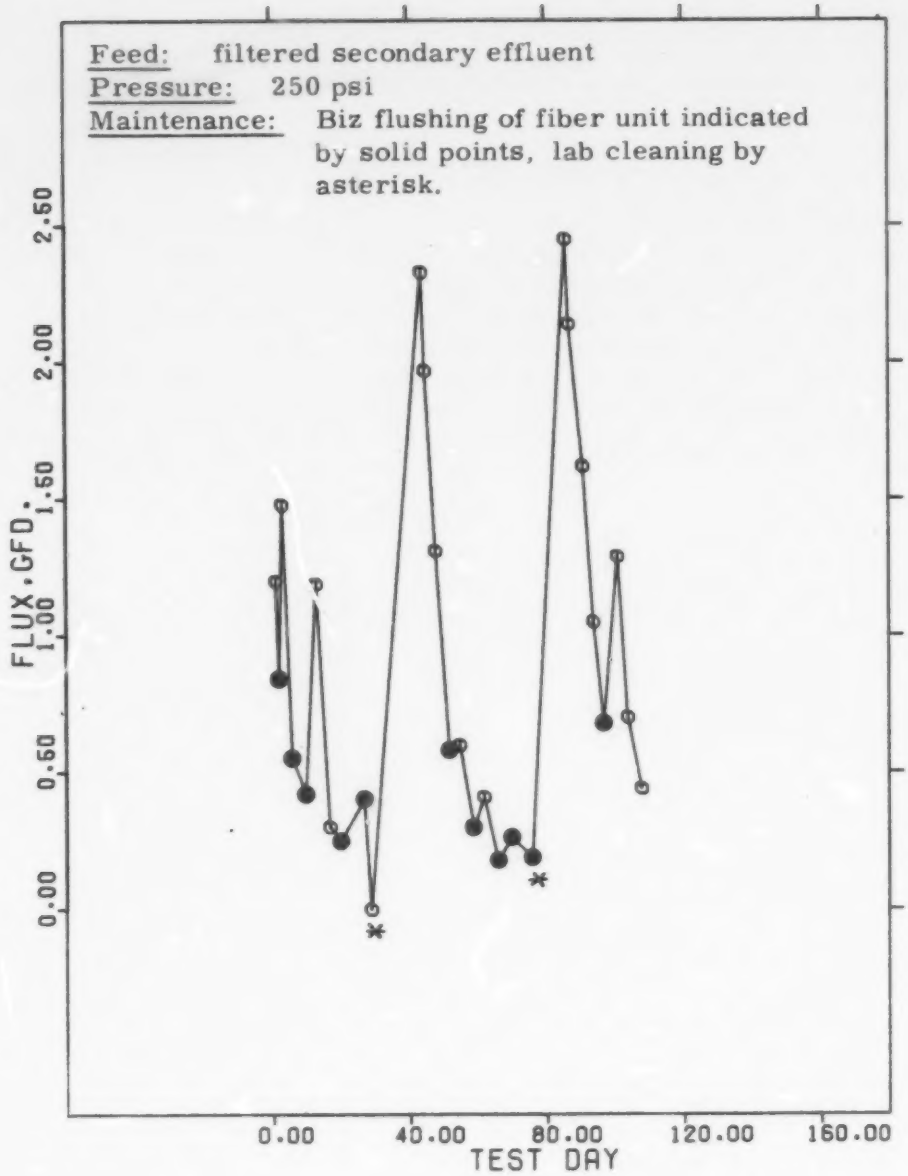


FIGURE 9A. VARIATION OF PRODUCT WATER FLUX WITH TIME-MODULE 0009

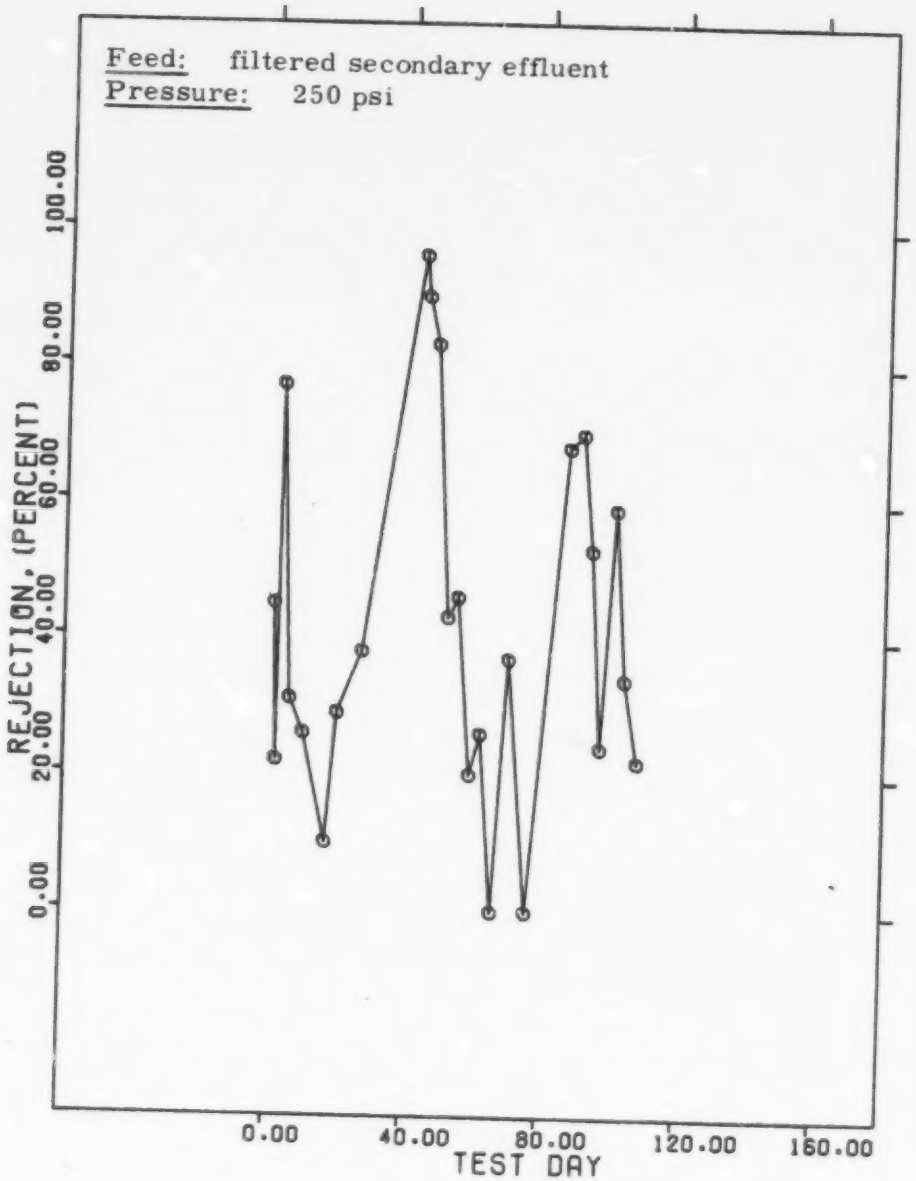


FIGURE 9B. VARIATION OF SODIUM ION REJECTION WITH TIME-MODULE D009

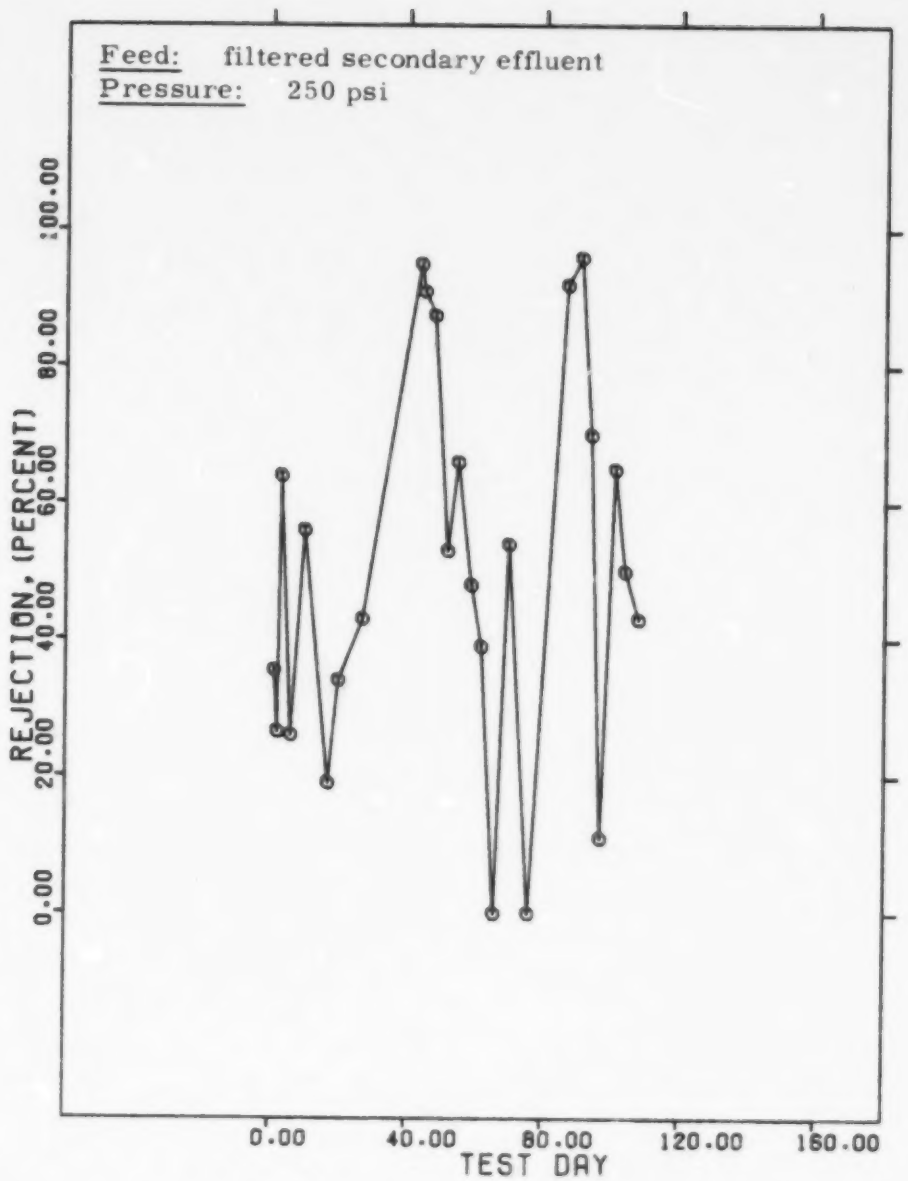


FIGURE 9C. VARIATION OF CHLORIDE ION REJECTION WITH TIME-MODULE D009

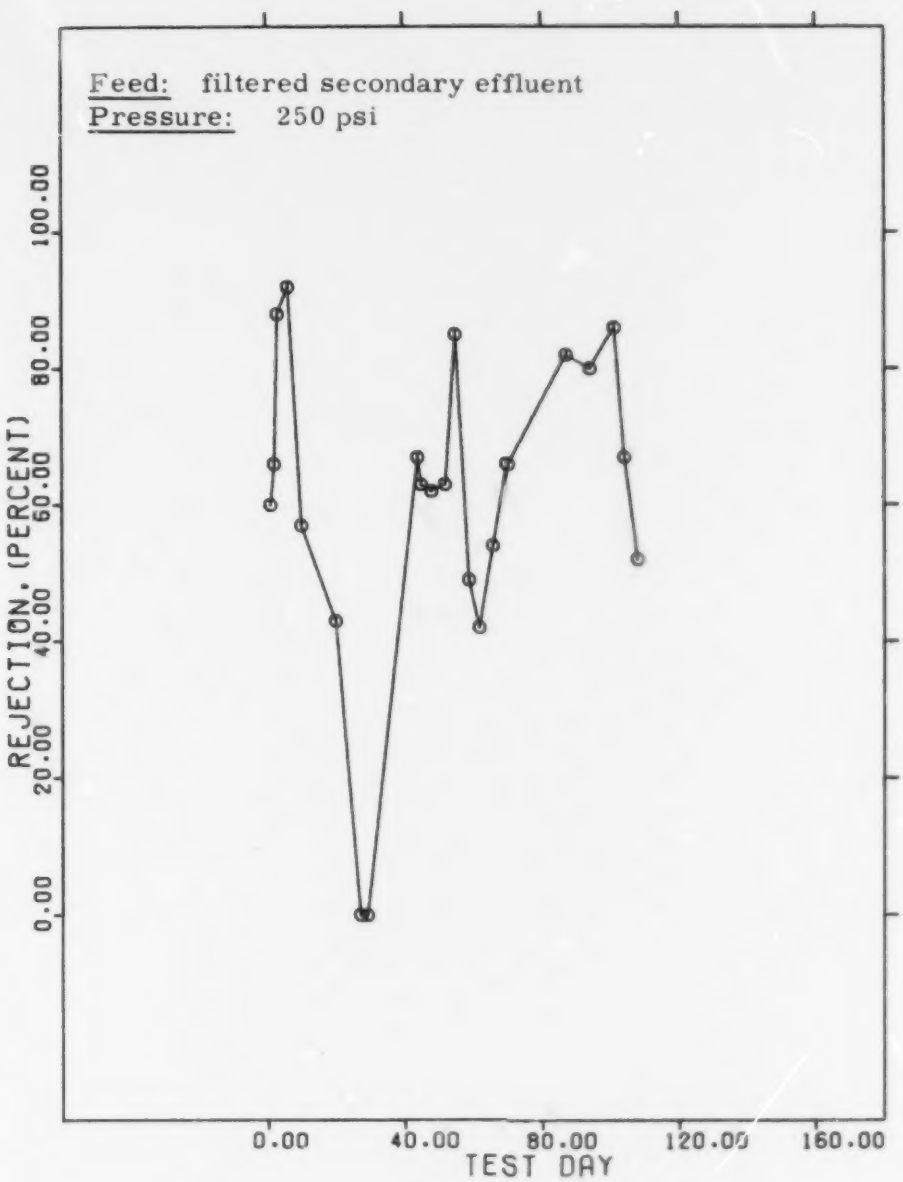


FIGURE 9D. VARIATION OF BOD REJECTION WITH TIME-MODULE D009

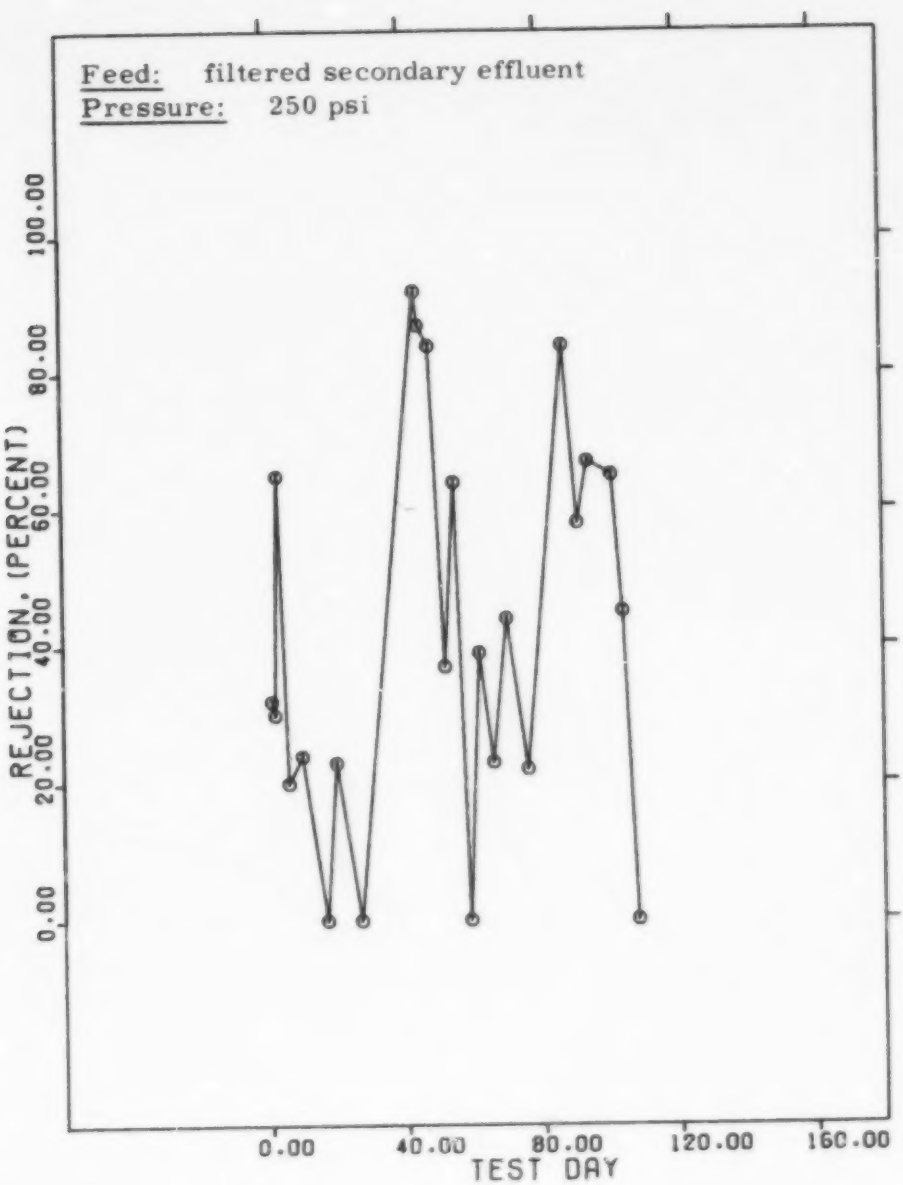


FIGURE 9E. VARIATION OF KJELDAHL NITROGEN REJECTION WITH TIME-MODULE D009

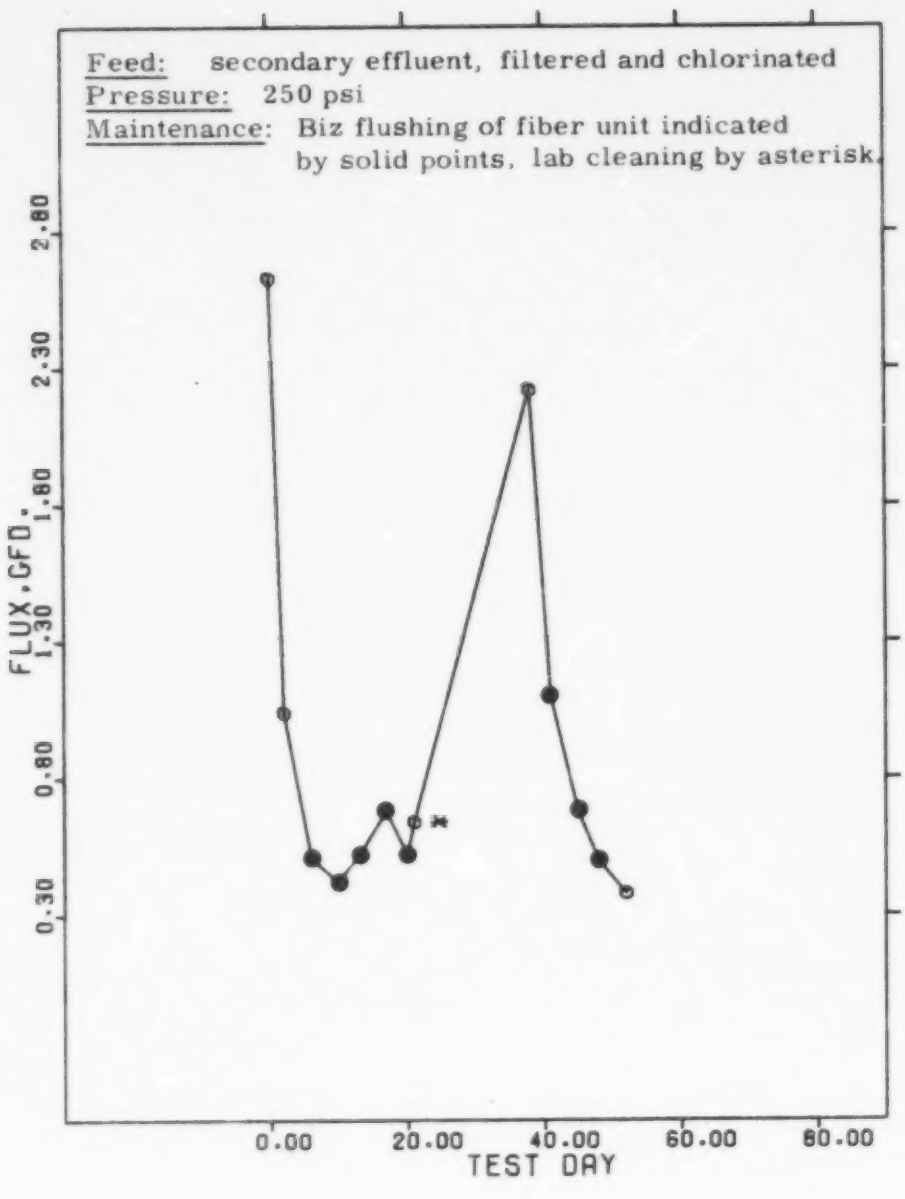


FIGURE 10A. VARIATION OF PRODUCT WATER FLUX WITH TIME-MODULE D010

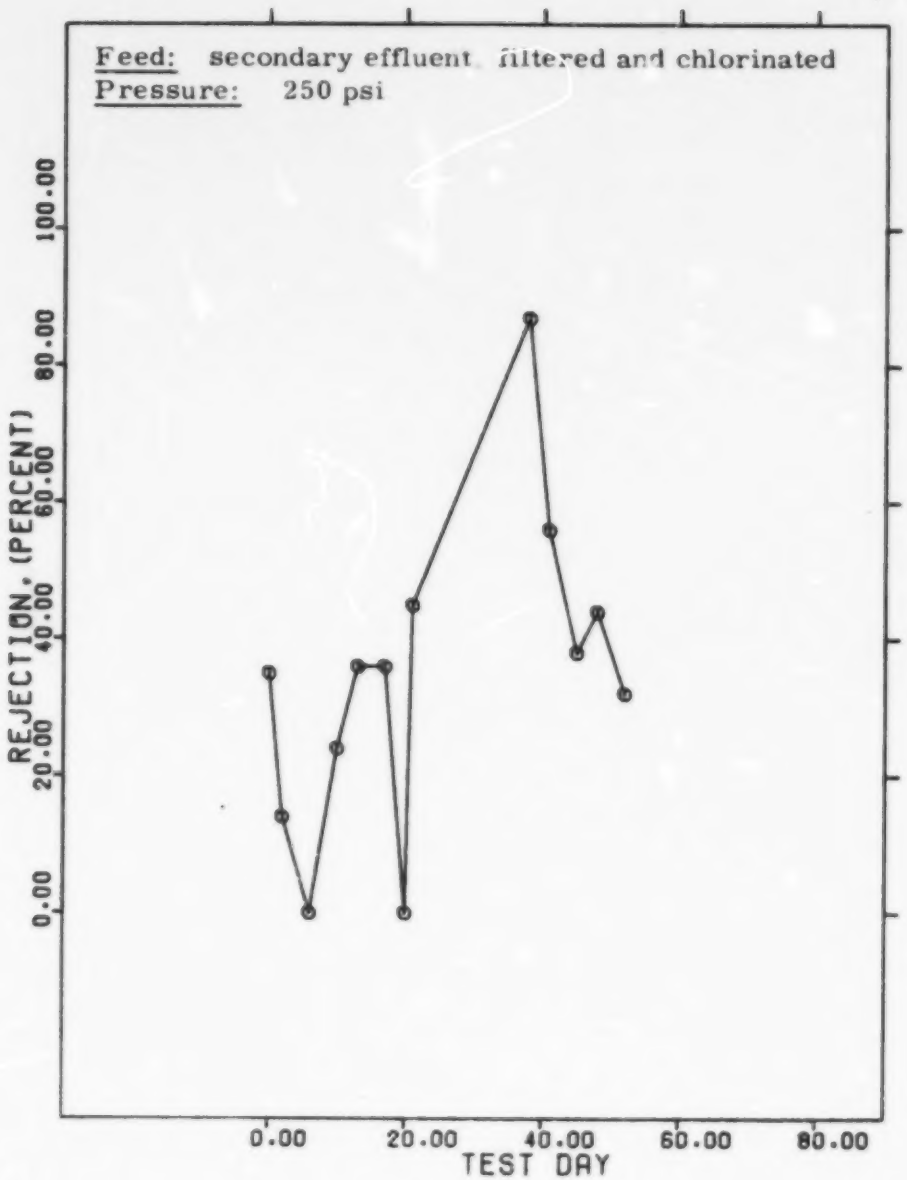


FIGURE 10B. VARIATION OF SODIUM ION REJECTION WITH TIME-MODULE D010

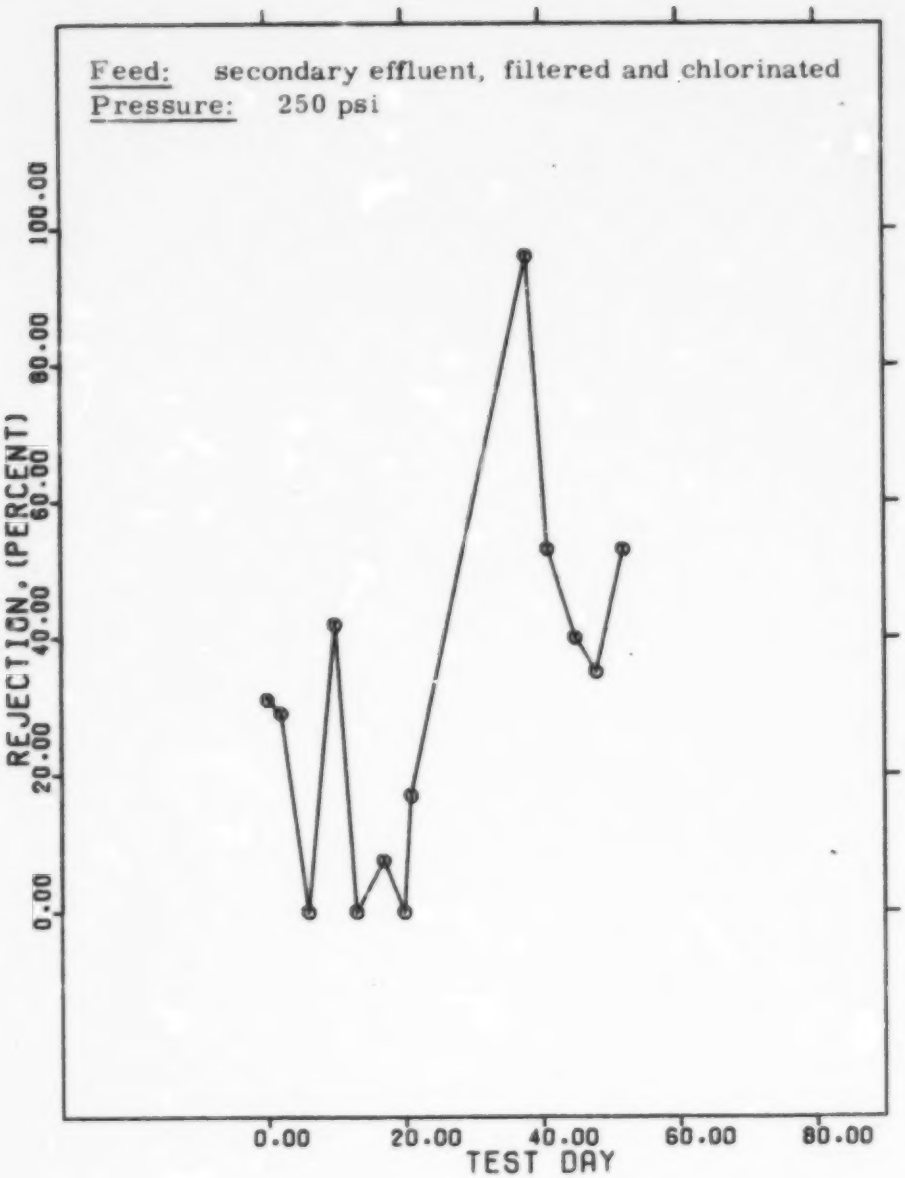


FIGURE 10C. VARIATION OF CHLORIDE ION REJECTION WITH TIME-MODULE D010

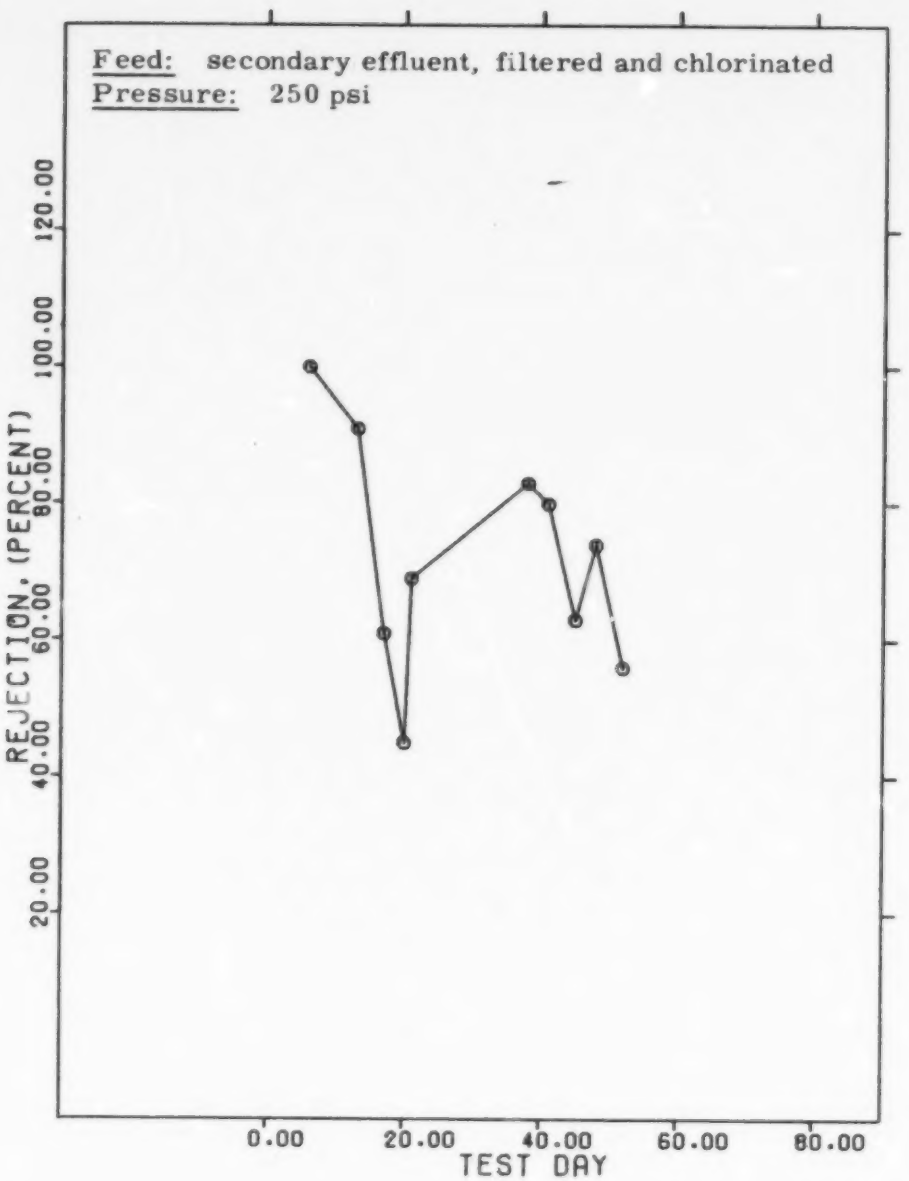


FIGURE 10D. VARIATION OF BOD REJECTION WITH TIME-MODULE D010

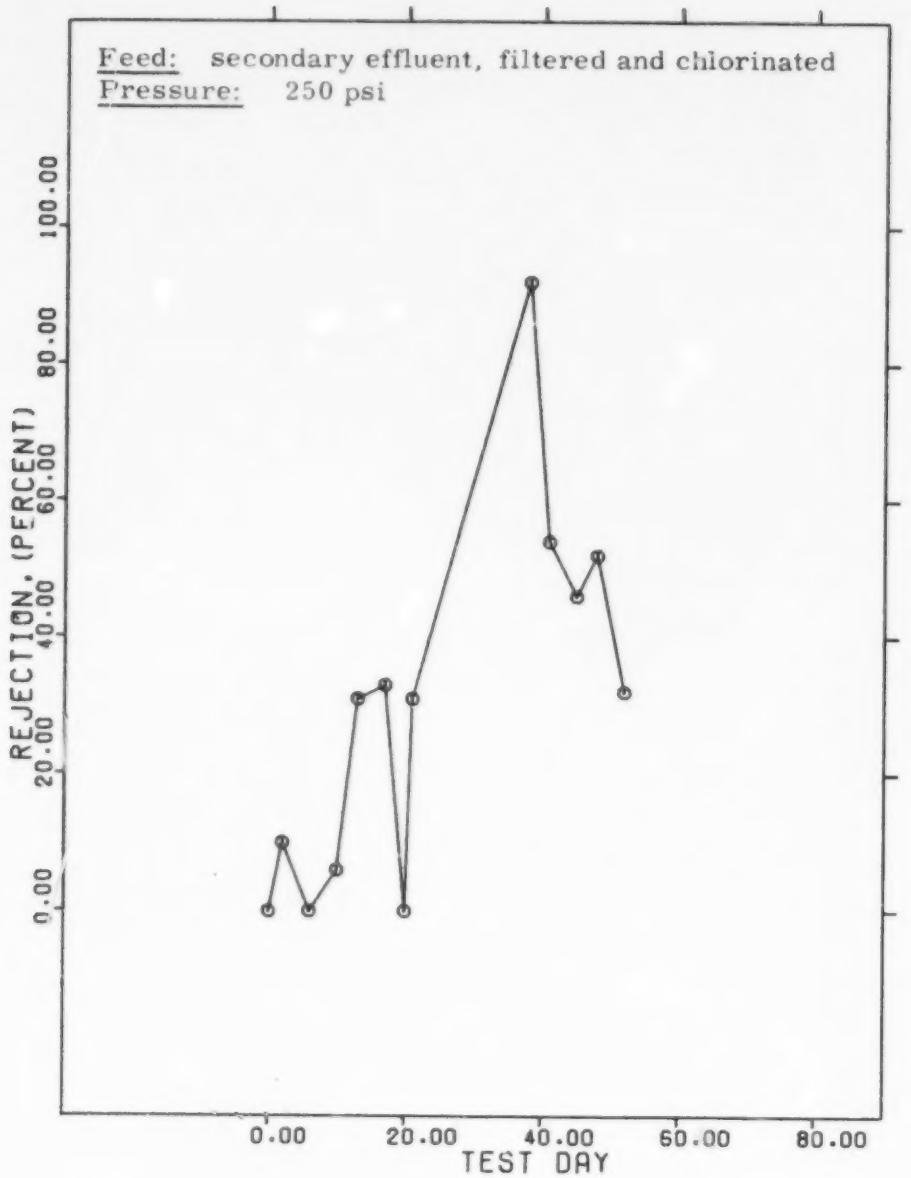


FIGURE 10E. VARIATION OF KJELDAHL NITROGEN REJECTION WITH TIME-MODULE D010

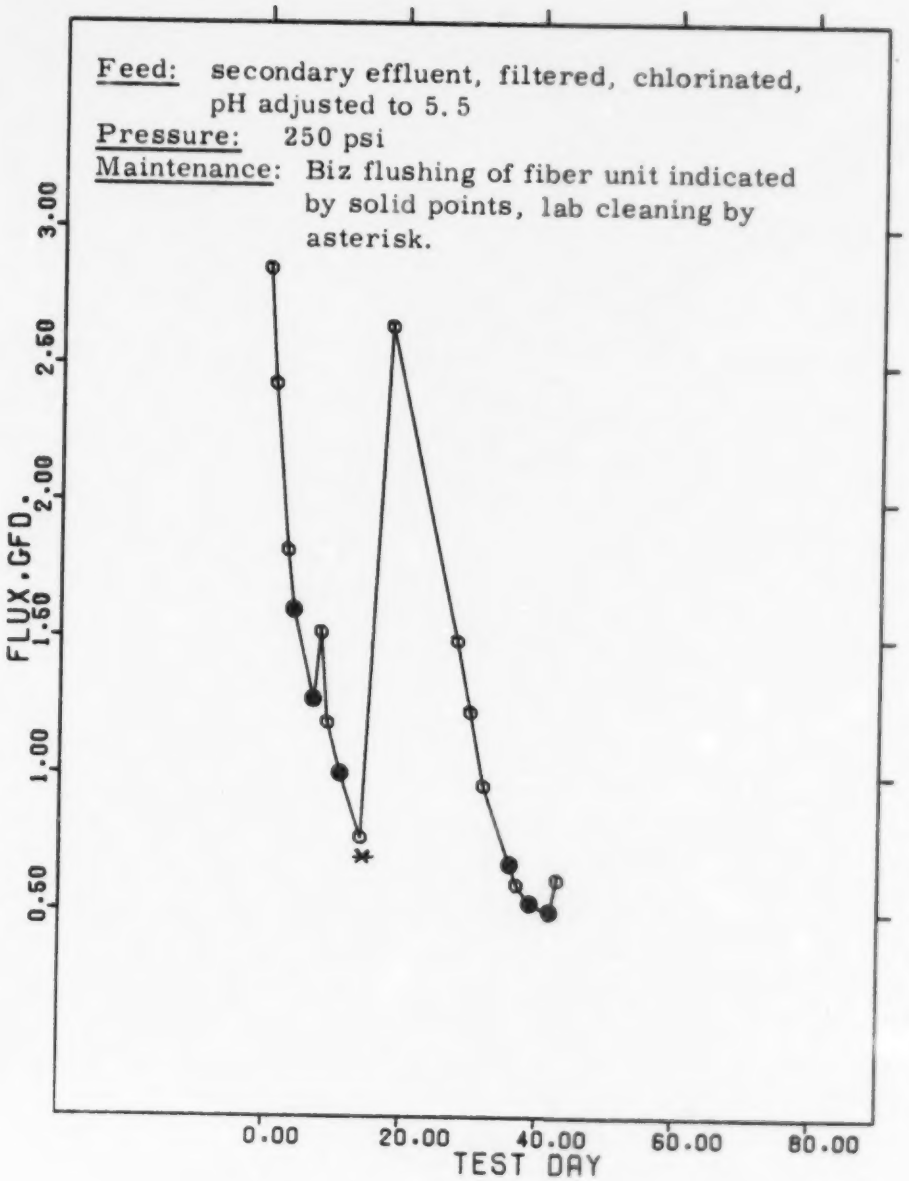


FIGURE 11A. VARIATION OF PRODUCT WATER FLUX WITH TIME-MODULE D008

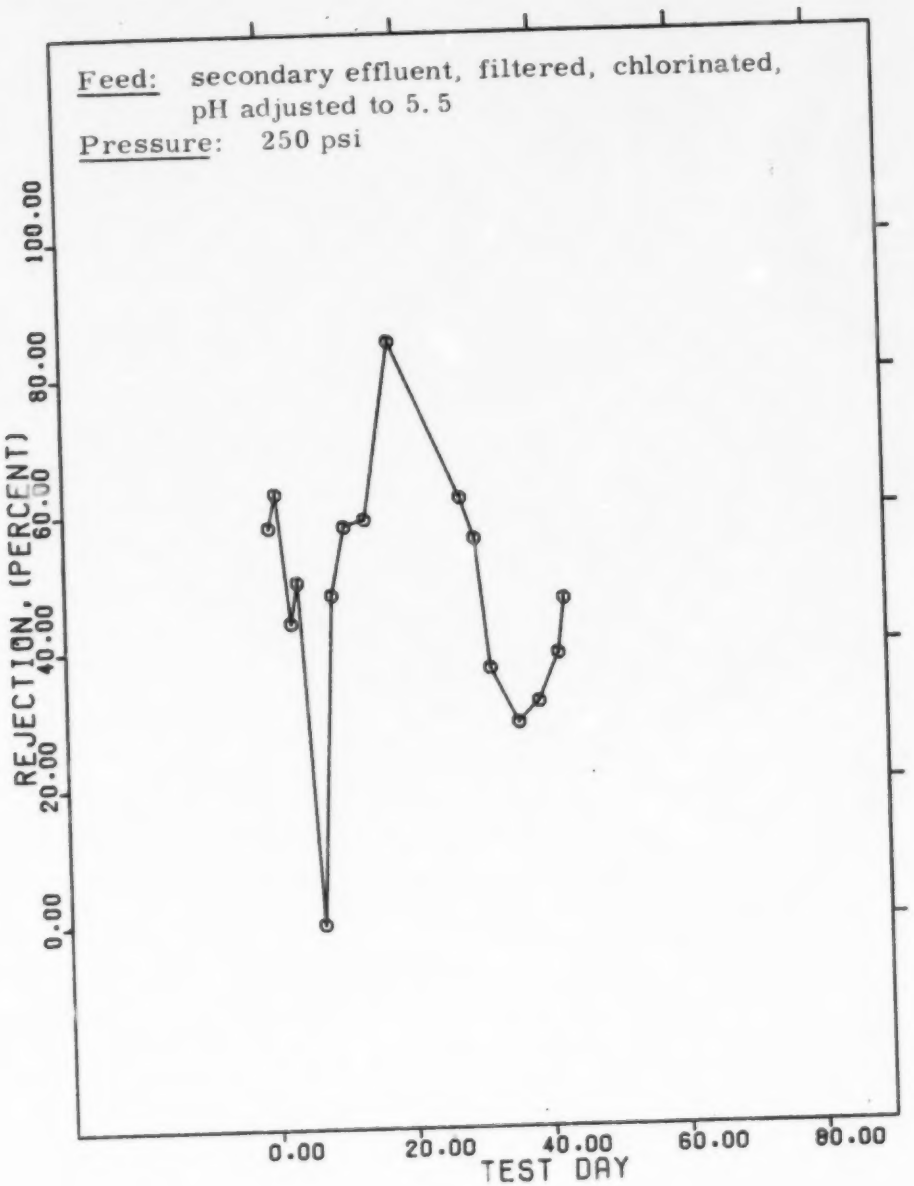


FIGURE 11B. VARIATION OF SODIUM ION REJECTION WITH TIME-MODULE D008

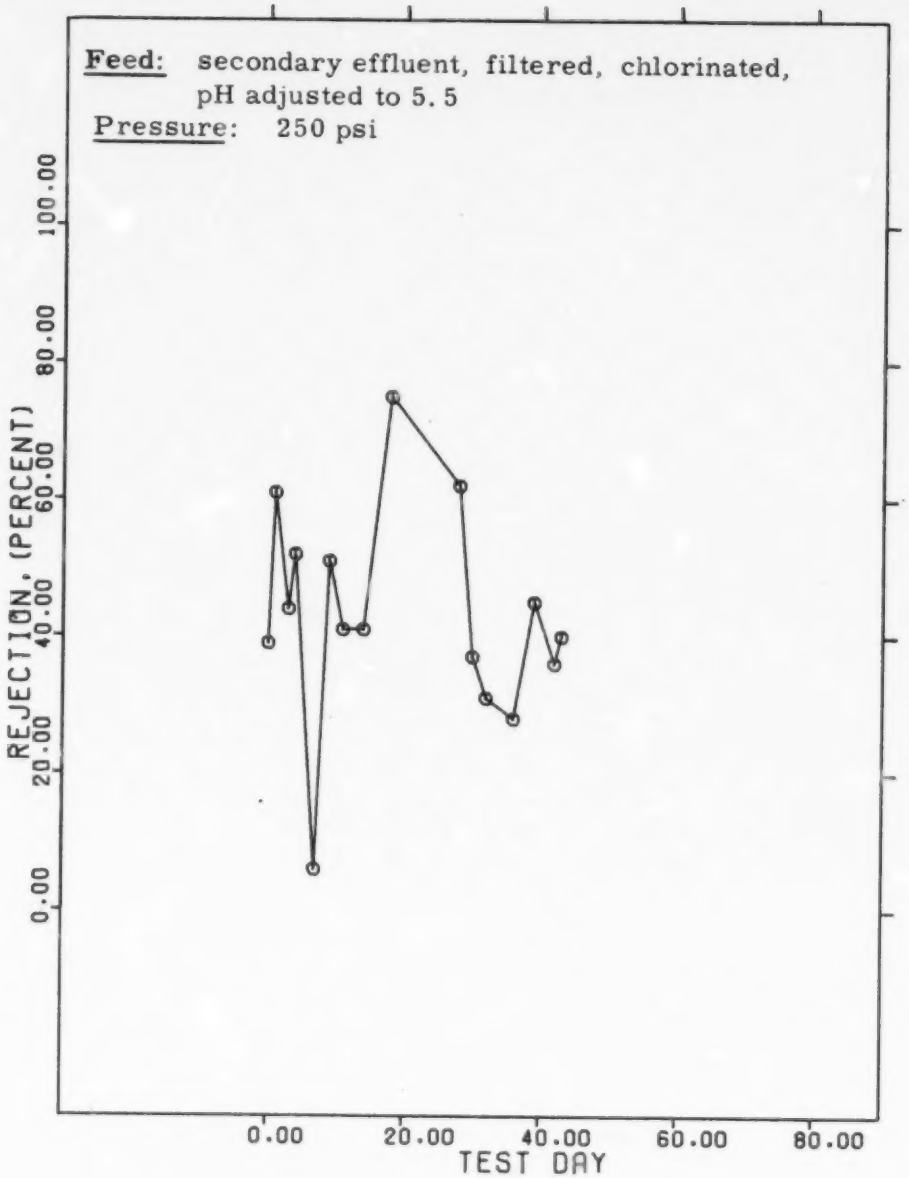


FIGURE 11C. VARIATION OF CHLORIDE ION REJECTION WITH TIME-MODULE D008

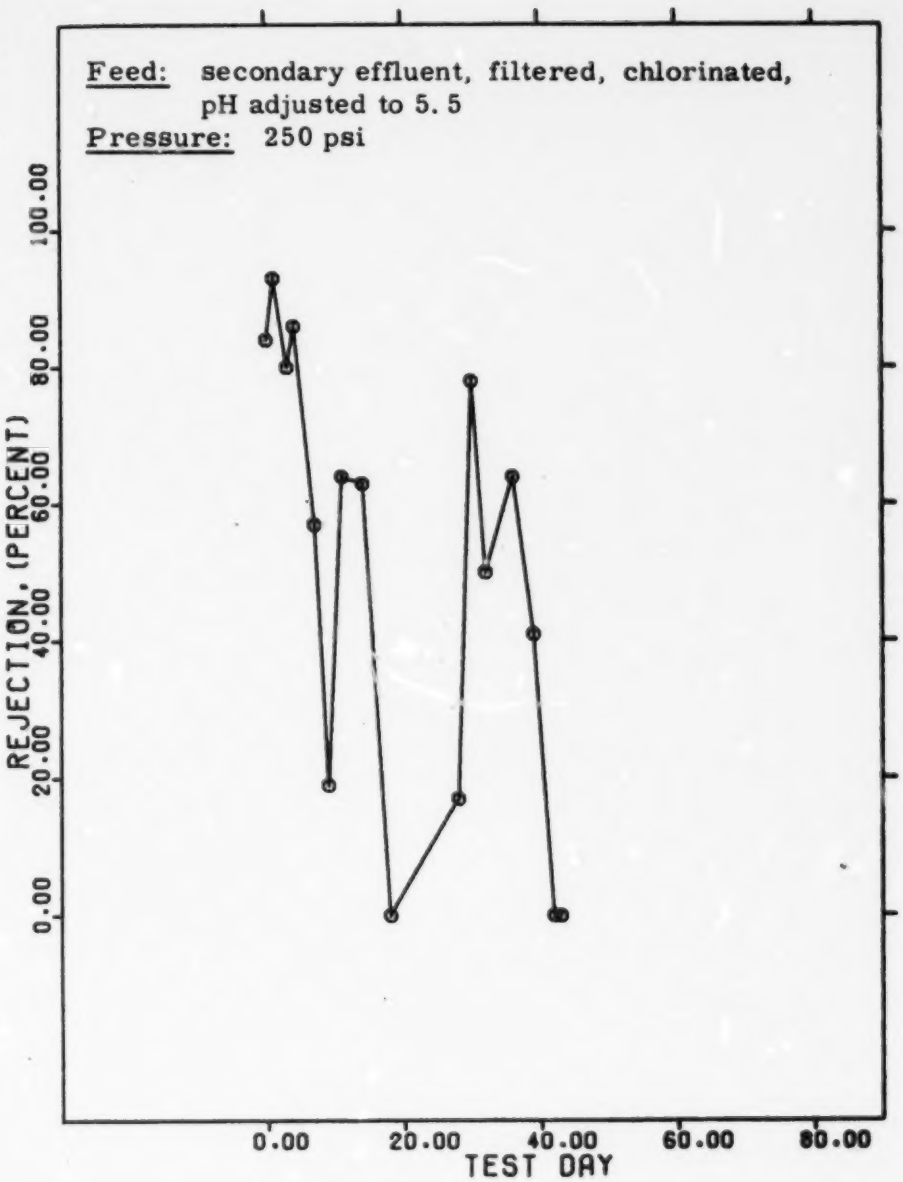


FIGURE 11D. VARIATION OF BOD REJECTION WITH TIME-MODULE D008

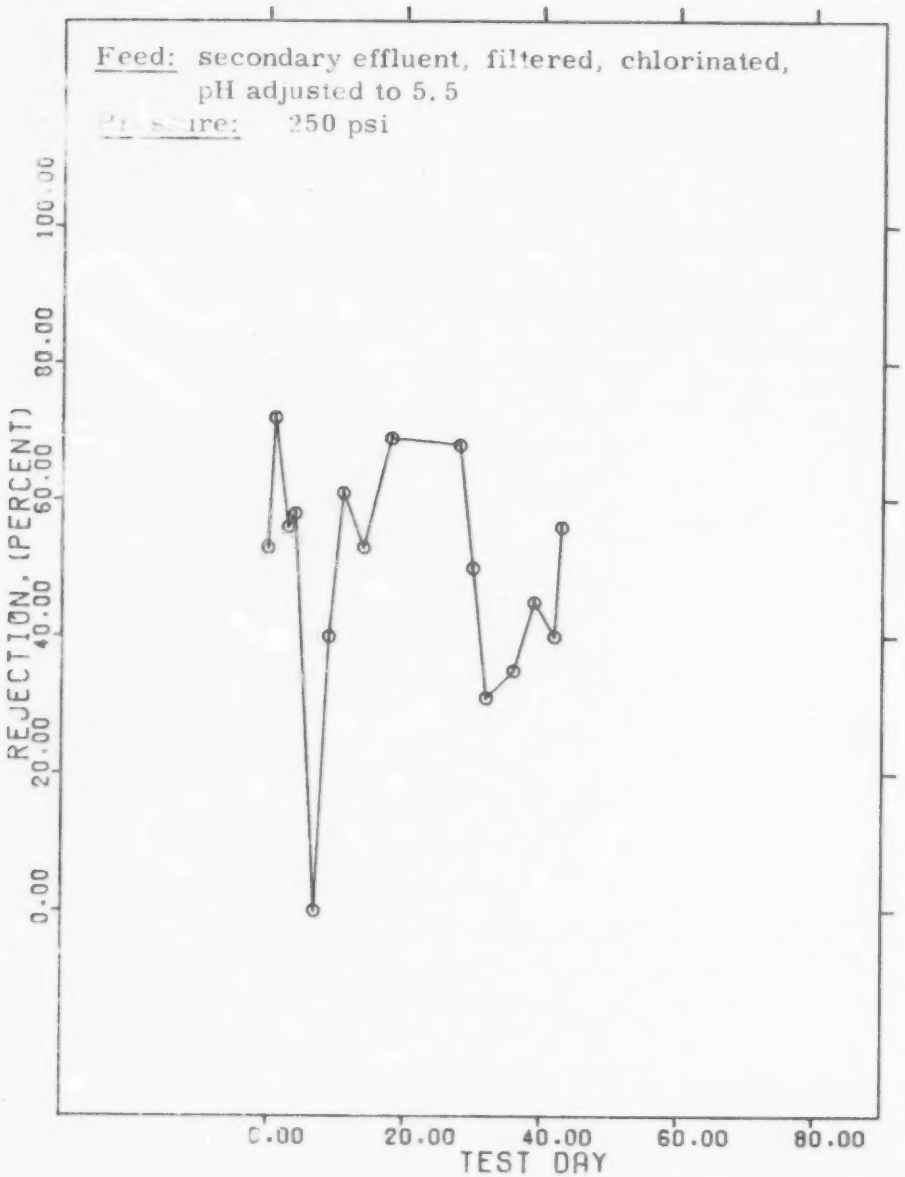


FIGURE 11E. VARIATION OF KJELDAHL NITROGEN REJECTION WITH TIME-MODULE D008

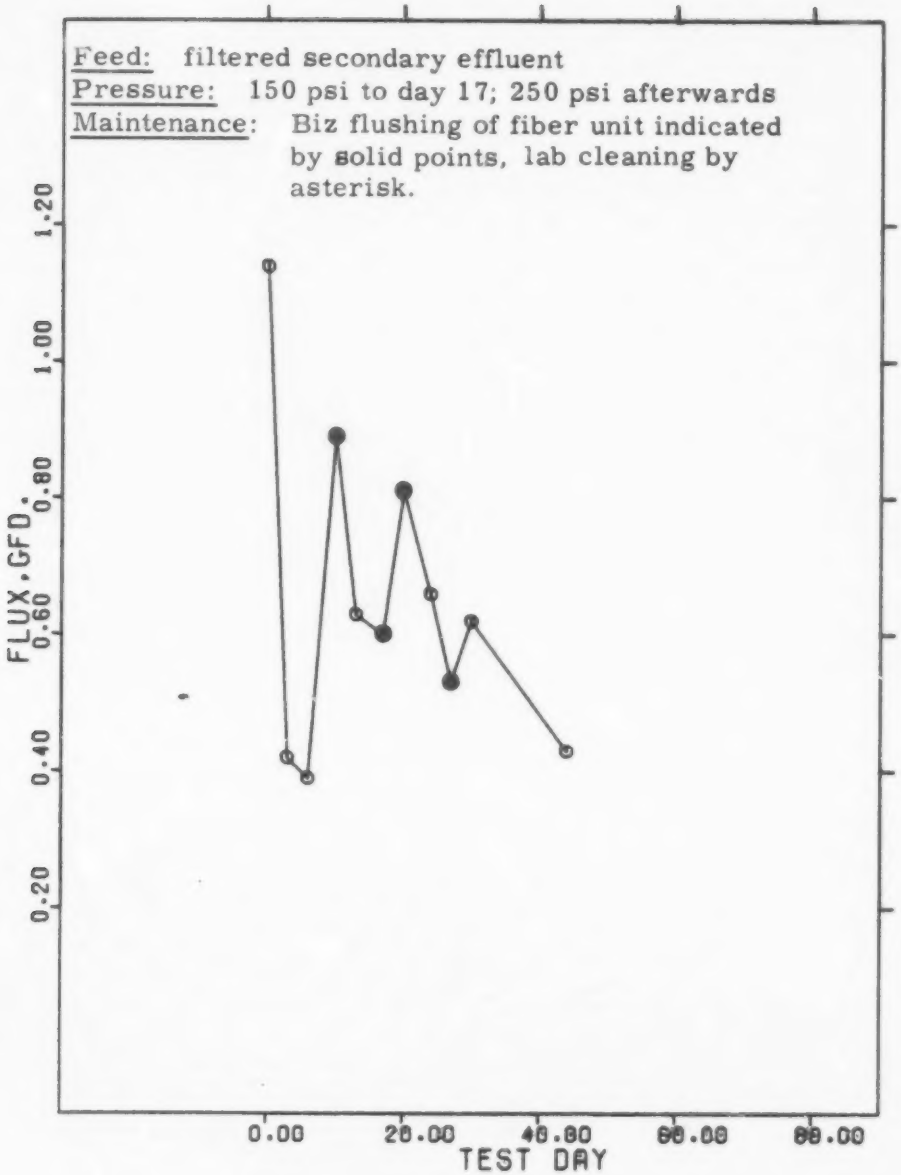


FIGURE 12A. VARIATION OF PRODUCT WATER FLUX WITH TIME-MODULE D0013-2

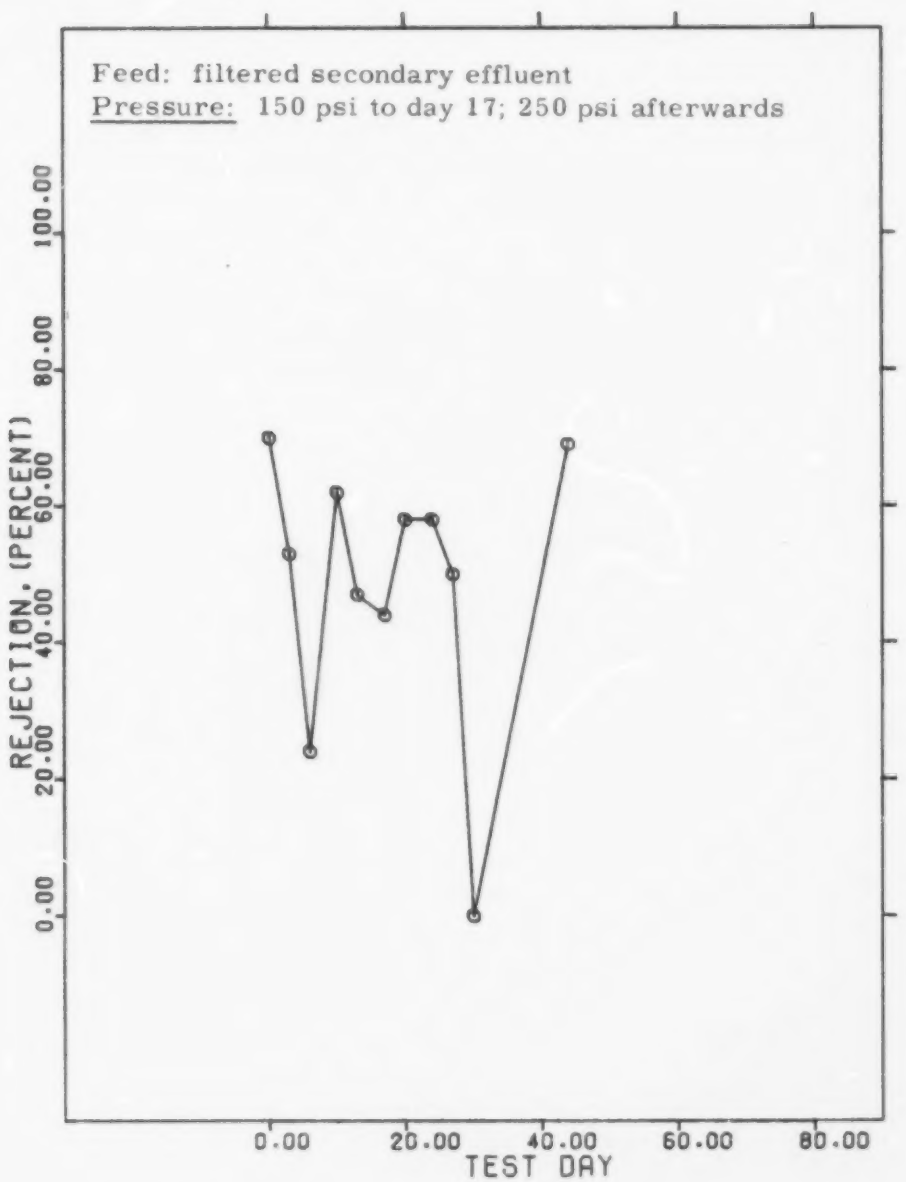


FIGURE 12B. VARIATION OF SODIUM ION REJECTION WITH TIME-MODULE D0013-2

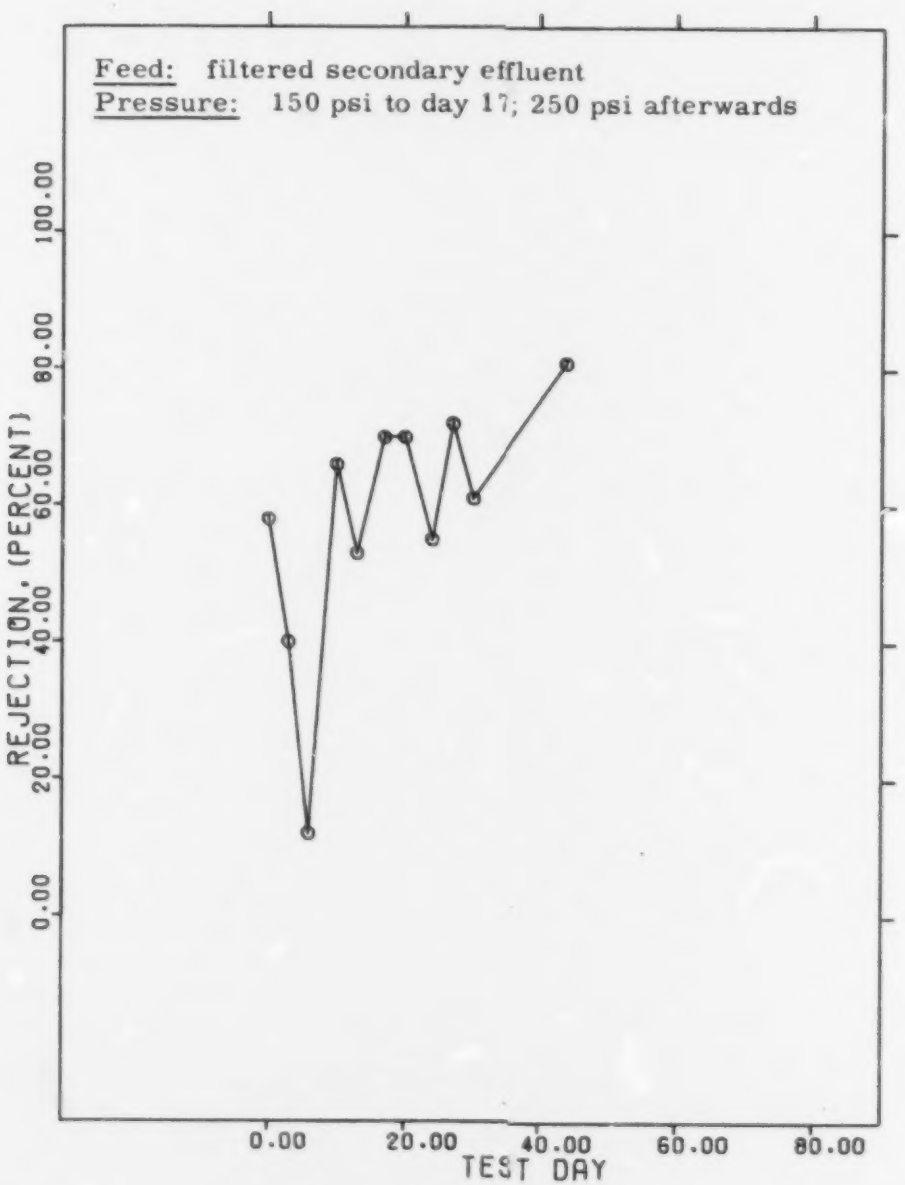


FIGURE 12C. VARIATION OF CHLORIDE ION REJECTION WITH TIME-MODULE D0013-2

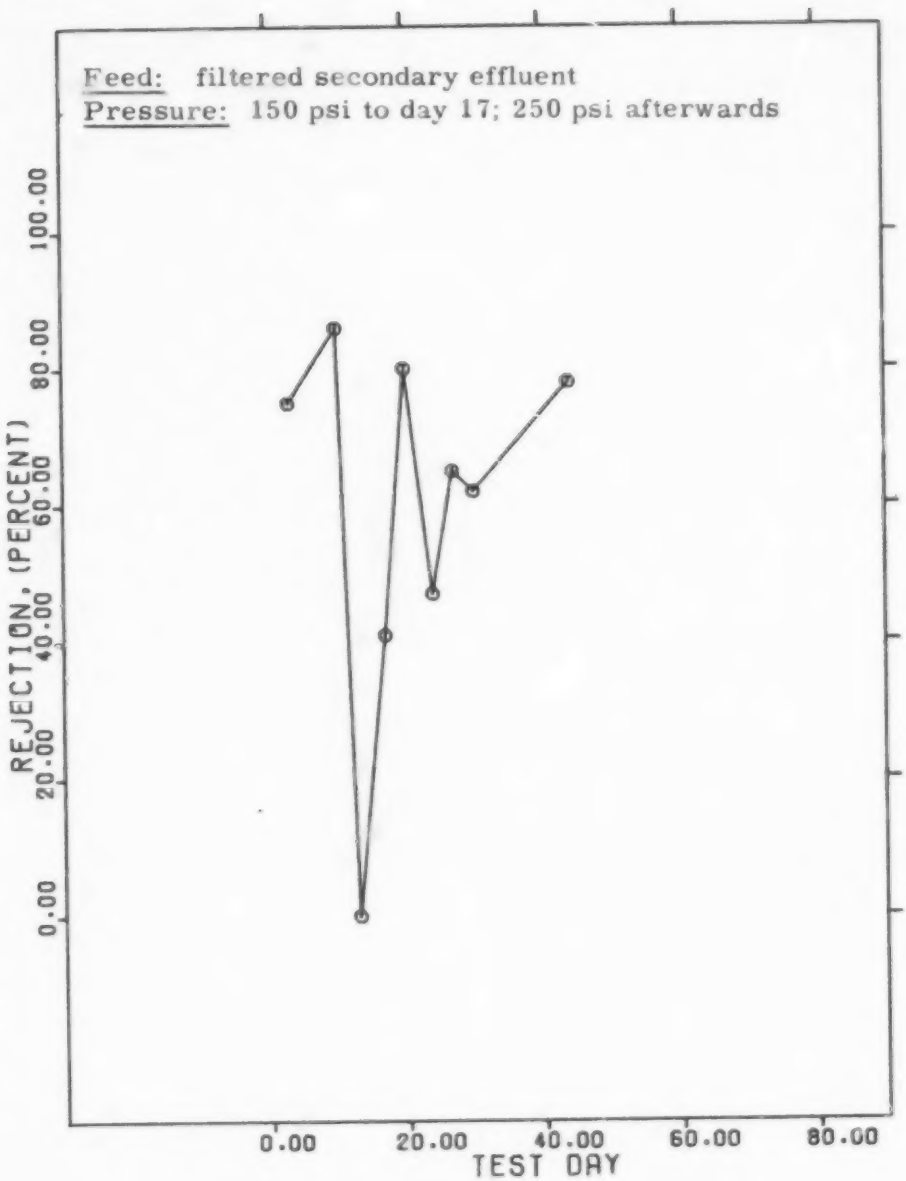


FIGURE 120. VARIATION OF BOD REJECTION WITH TIME-MODULE DOO[illegible]3-2

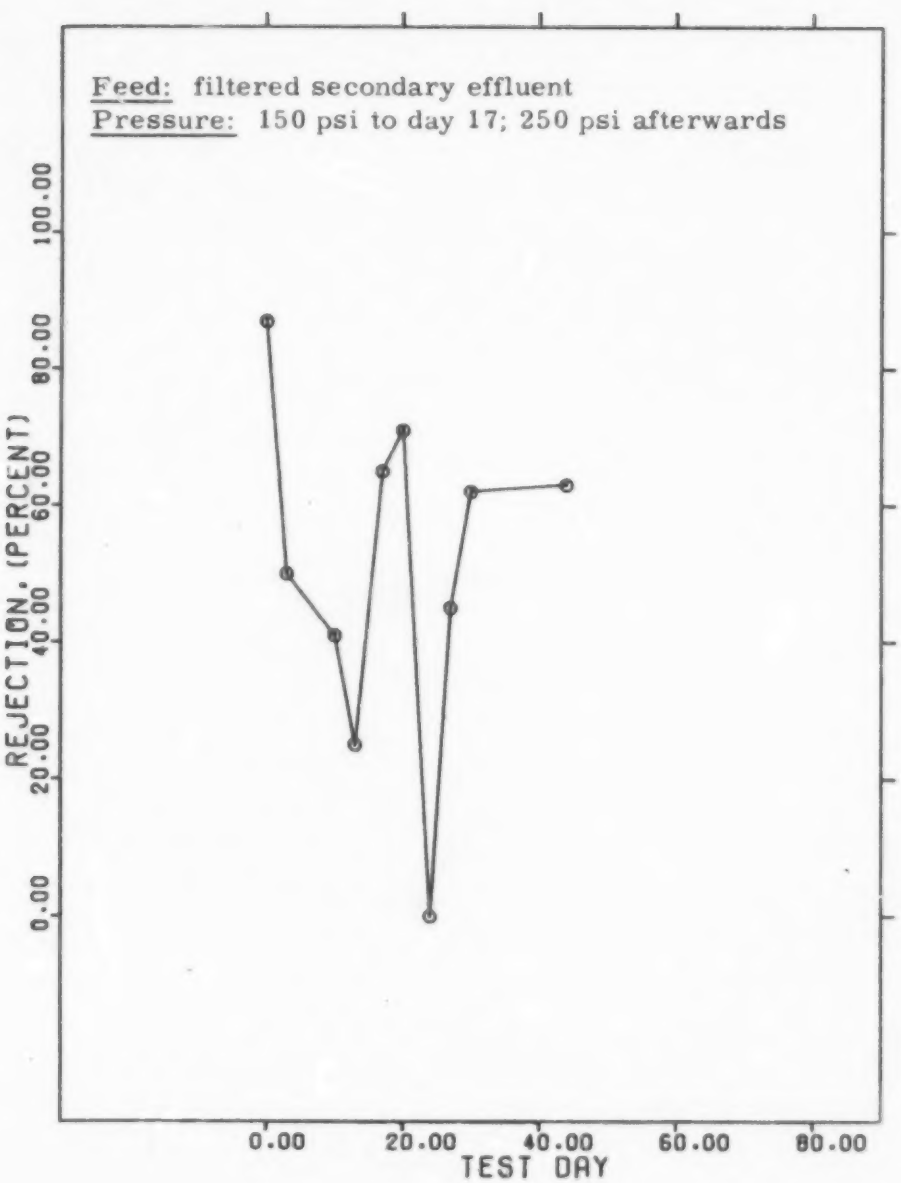


FIGURE 12E. VARIATION OF KJELDAHL NITROGEN REJECTION WITH TIME-MODULE DD013-2

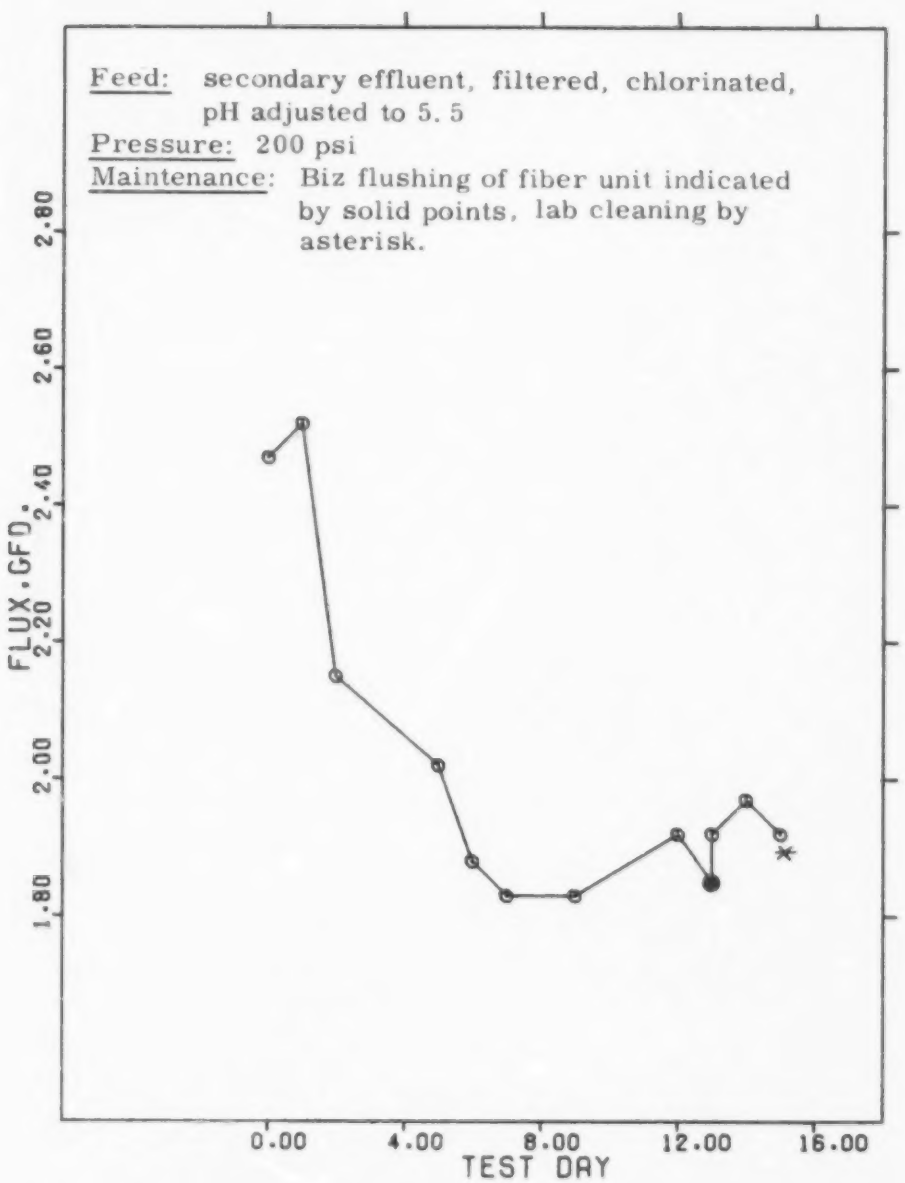


FIGURE 13A. VARIATION OF PRODUCT WATER FLUX WITH TIME-MODULE WA001

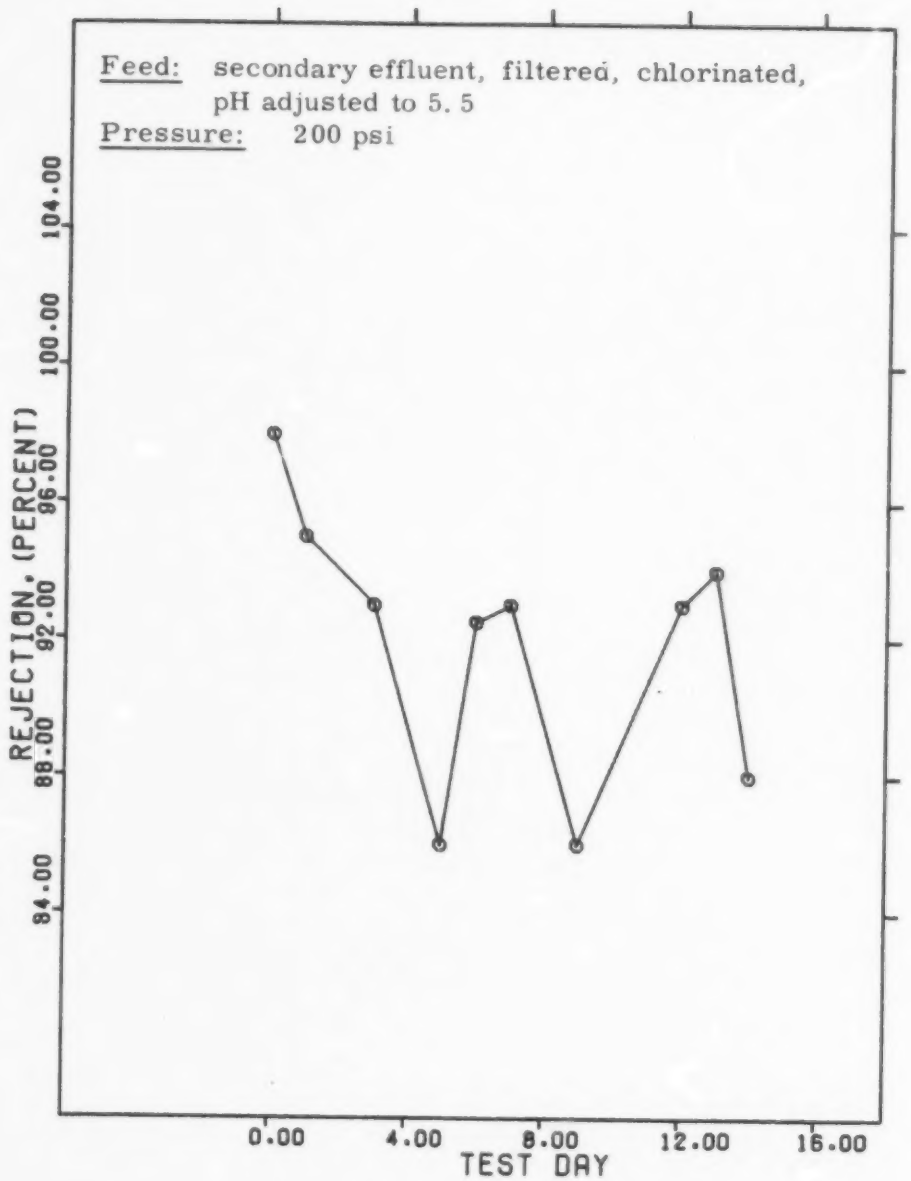


FIGURE 13B. VARIATION OF SODIUM ION REJECTION WITH TIME-MODULE WA001

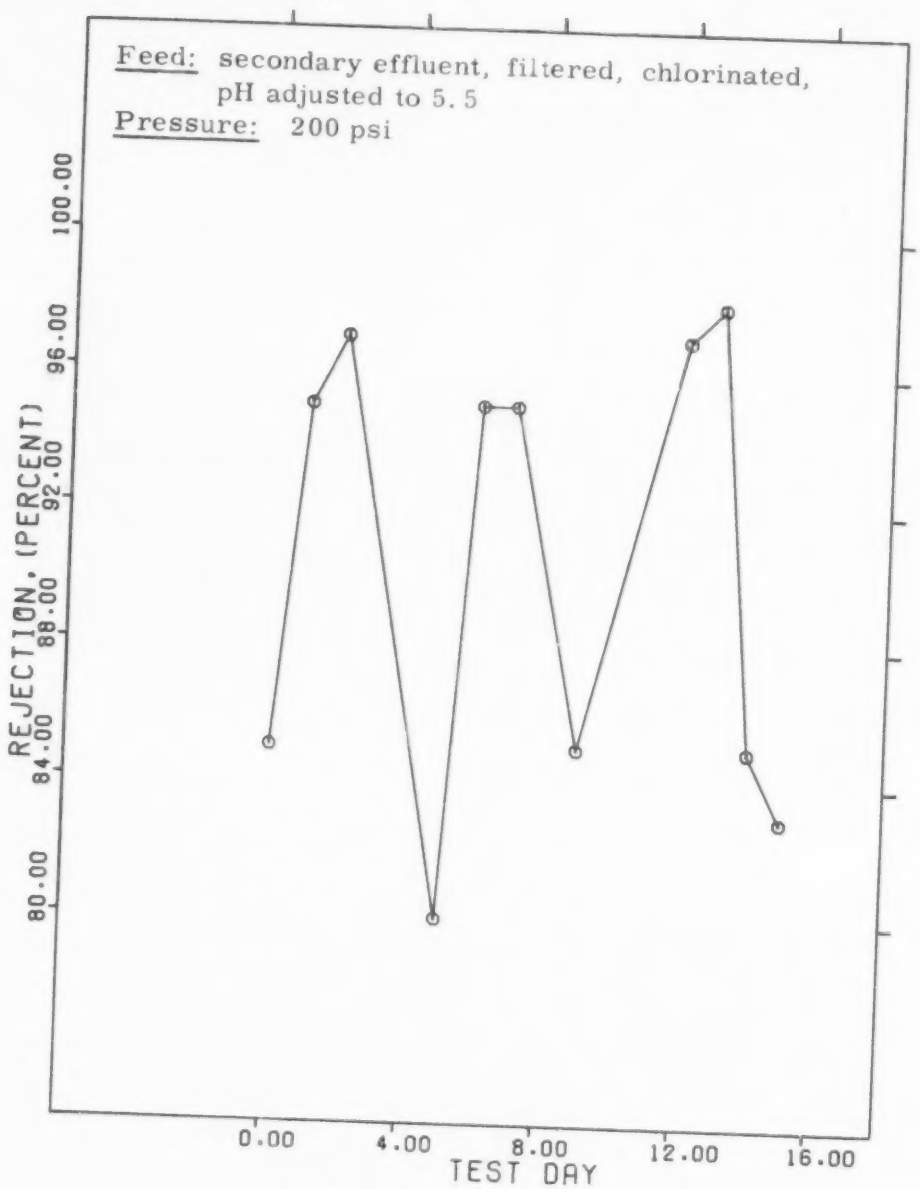


FIGURE 13C. VARIATION OF CHLORIDE ION REJECTION WITH TIME-MODULE WA001

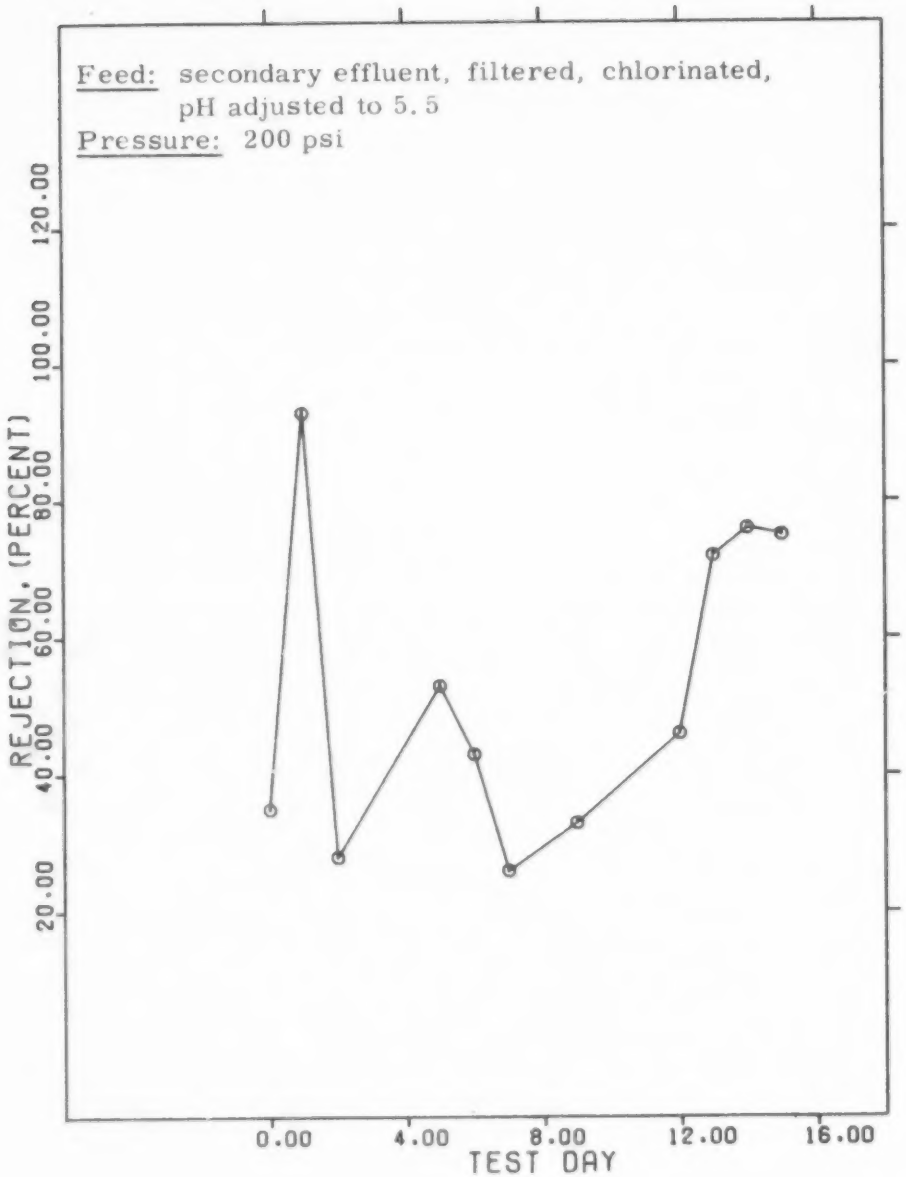


FIGURE 13D. VARIATION OF BOD REJECTION
WITH TIME-MODULE WA001

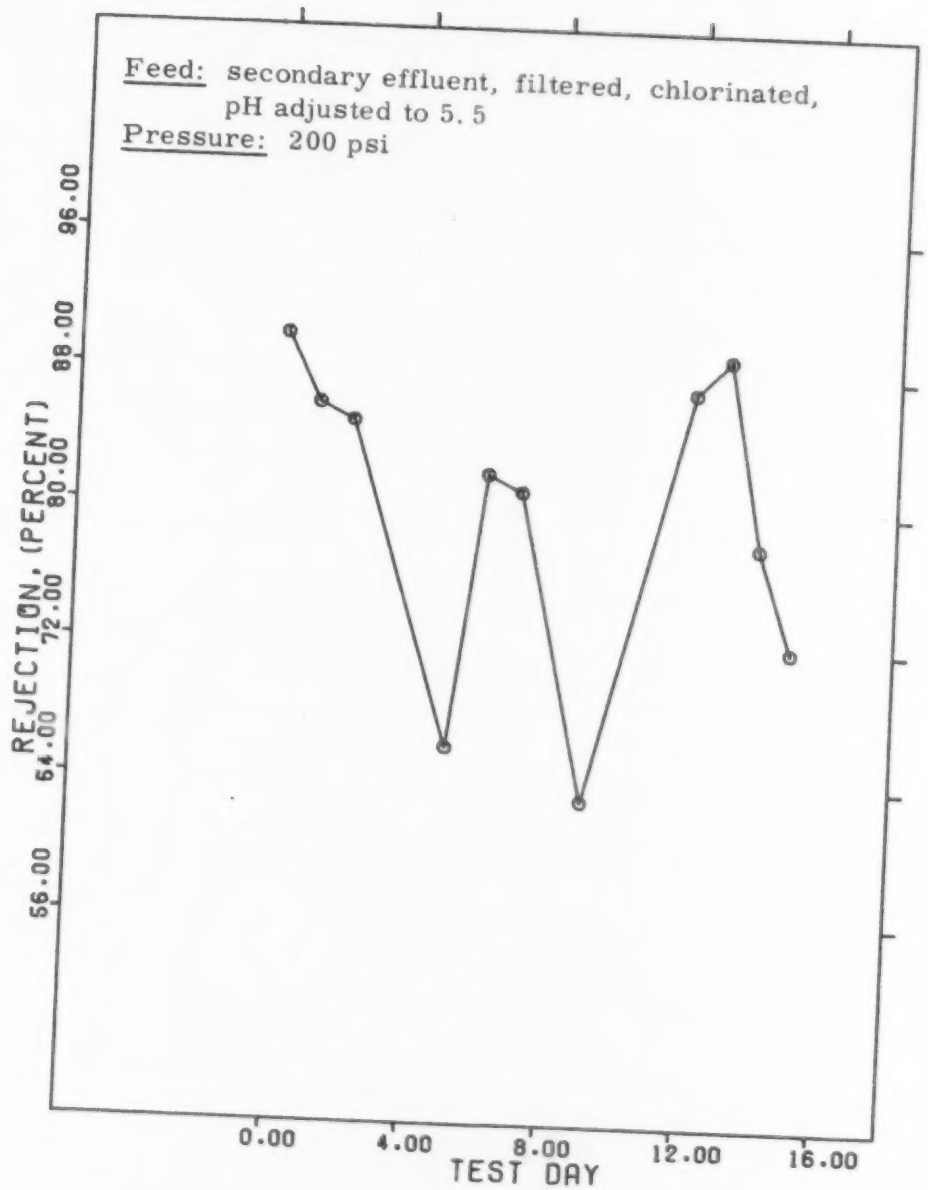


FIGURE 13E. VARIATION OF KJELDAHL NITROGEN REJECTION WITH TIME-MODULE WA001

VIII ACKNOWLEDGMENTS

Personnel at Chemstrand Research Center, Inc. who participated directly in this program were J. D. Bashaw (Principal Investigator from 10-70 to 2-71), J. K. Lawson (Principal Investigator from 2-71 to 12-71), J. C. Berry, E. S. Gothard, R. L. Leonard, R. F. Cole, L. C. Locust, and M. C. Readling. Program Manager was T. A. Orofino. EPA Project Officer was John M. Smith.

Experimental field work was carried out in laboratories of the University of North Carolina Wastewater Research Center, at Chapel Hill, North Carolina. We wish to thank the personnel of this facility for the use of space and for their cooperation on many occasions. Particular thanks are due to Dr. James C. Brown, manager of the Wastewater Research Center, Dr. Linda Little, Dr. Don Francisco, Mr. William Walker, and Mr. John Street. Some of the analyses which we required were performed either at the Wastewater Research Center, or else were conducted by University of North Carolina laboratories for us at the request of Dr. Brown and Mr. Walker. These included BOD, Kjeldahl nitrogen, ammonia nitrogen, phosphate, organic and inorganic carbon, nitrate, and nitrite. When the sand filter was installed, we were able to arrange for Mr. Street to backwash it for us on a regular basis. On the few occasions when some of our equipment misfunctioned, various members of their staff were prompt to notify us.

IX REFERENCES

1. S. Loeb and S. Sourirajan, University of California (Los Angeles) Eng. Dept., Report No. 60-60, July 1960.

2. T. A. Orofino et al., Office of Saline Water Research and Development Progress Report No. 549, May 1970.

3. H. B. Hopfenberg, Department of Chemical Engineering, North Carolina State University, Raleigh, N. C., private communication. See also A. S. Michaels, Chem. Eng. Progs. 64, No. 12, 31 (1968)

4. Ulrich Merten, "Desalination by Reverse Osmosis," U. Merten, Ed., The M. I. T. Press, 1966 (Chapter 2).

5. Work conducted under Contract 14-30-2773, Office of Saline Water, U. S. Department of the Interior to Monsanto Research Corporation.

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